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AMERICAN

CHEMICAL JOURNAL

IRA REMSEN
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ASSISTANT EDITOR

VOL. XLVIII.—JULY–DECEMBER, 1912

BALTIMORE: THE EDITOR

ESCHENBACH PRINTING COMPANY, PRINTERS,
EASTON, PA.

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CONTENTS OF VOL. XLVIII

No. 1

CONTRIBUTIONS FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF CINCINNATI:

The Beckmann Rearrangement of Hydroxamic Acids. By Lauder William Jones 1

THE OSMOTIC PRESSURE OF CANE SUGAR SOLUTIONS AT HIGH TEMPERATURES. By H. N. Morse, W. W. Holland, C. N. Myers, G. Cash and J. B. Zinn 29

REVIEWS

Cocoa and Chocolate, their Chemistry and Manufacture . . . 95
Die elektrochemischen Verfahren der chemischen Gross-Industrie . 97
Das Hydrosulfit 98
Stand und Wege der analytischen Chemie 99
A Handbook of Organic Analysis, Qualitative and Quantitative 100
The Chemistry of the Radio Elements 101
Physico-chemical Calculations 102
A Text-Book of Inorganic Chemistry 102
Les Nouveautés Chimiques pour 1911 102

No. 2

CONTRIBUTIONS FROM THE SHEFFIELD LABORATORY OF YALE UNIVERSITY:

CC.—*Hydantoins: The Action of Potassium Thiocyanate on Asparagine.* By Treat B. Johnson and Herbert H. Guest 103

METHODS FOR DETERMINING NEO- AND ALLOCHLOROPHYLL IN THE PRESENCE OF ONE ANOTHER. By C. A. Jacobson and L. Marchlewski 111

POTENTIALS OF ZINC IN ALCOHOLIC SOLUTIONS OF ZINC CHLORIDE. By Frederick H. Getman and Vernette L. Gibbons . . . 124

A STUDY OF THE REFRACTIVE INDICES OF SOLUTIONS OF THE CADMIUM HALIDES. By Frederick H. Getman and Helen T. Gilroy. 138

A STUDY OF THE CHANGE FROM VIOLET TO GREEN IN SOLUTIONS OF CHROMIUM SULPHATE. By Minnie A. Graham . . . 145

REVIEWS

Technical Methods of Chemical Analysis 190
A Dictionary of Applied Chemistry 191
Die Chemie der Cellulose 192
The Chemistry of Bread-making 194
An Experimental Course of Physical Chemistry 195

251710

Die Methoden der Massanalyse 196
E. Merck's Annual Report of Recent Advances in Pharmaceutical Chemistry and Therapeutics 196
Prüfung der chemischen Reagentien auf Reinheit 196

No. 3

CONTRIBUTIONS FROM THE SHEFFIELD LABORATORY OF YALE UNIVERSITY:
    CCI.—*Desmotropism in the Pseudothiohydantoins.* By Treat B. Johnson and Joseph A. Ambler 197
THE REACTION BETWEEN ORGANIC MAGNESIUM COMPOUNDS AND CINNAMYLIDENE ESTERS. By Marie Reimer and Grace Potter Reynolds 206
ACTION OF HEAT ON *p*-SULPHAMIDO-*o*-TOLUIC ACID. By John W. Nowell 223
VELOCITY COEFFICIENTS OF THE REACTION BETWEEN ETHYL IODIDE AND SILVER NITRATE IN ETHYL AND METHYL ALCOHOLS AND MIXTURES OF THESE SOLVENTS. By J. N. Pearce and Otis M. Weigle 243

REVIEWS

A Dictionary of Applied Chemistry 259
Die Fabrikationen von Bittersalz und Chlormagnesium . . . 261
Allen's Commercial Organic Analysis 261
Materials for Permanent Painting 262
Tests of the Absorptive and Permeable Properties of Portland Cement Mortars and Concretes 263
Notions Fondamentales d'Analyse Qualitative 264
Die chemischen Grundlehren nach Menge, Mass und Zeit . . 265
Laboratory Exercises in Physical Chemistry 265

No. 4

ON THE ACTION OF AQUEOUS SOLUTIONS OF ACIDS ON ALKENES. By Arthur Michael and Roger F. Brunel 267
CONTRIBUTIONS FROM THE SHEFFIELD LABORATORY OF YALE UNIVERSITY:
    CCII.—*Researches on Pyrimidines: The Action of Hydroxylamine on 4-Methyl-6-oxypyrimidine-2-oxalothioglycollic Acid. β-Mercapto-α-oximidopropionic Acid.* By Treat B. Johnson and Norman A. Shepard . . . 279
    CCIII.—*Researches on Pyrimidines: The Action of Potassium Thiocyanate on Primary Halides.* By Treat B. Johnson and Arthur J. Hill 296
    CCIV.—*Researches on Pyrimidines: The Oximes of Some Thioglycollide Compounds and their Behavior on Reduction.* By Treat B. Johnson and Robert C. Moran . 307

A STUDY OF THE CONDUCTIVITY AND DISSOCIATION OF CERTAIN ORGANIC ACIDS AT 35°, 50° AND 65°. By E. P. Wightman and Harry C. Jones 320
ON THE MECHANISM OF ORGANIC REACTIONS. By S. F. Acree . . 352

OBITUARY

Paul Émile Lecoq de Boisbaudran 381

REVIEWS

Messungen elektromotorischer Kräfte galvanischer Ketten mit wässerigen Elektrolyten 382
Outlines of Organic Chemistry 382
Erratum 382

No. 5

THE COPPER COMPLEXES OF AMINO ACIDS, PEPTIDES AND PEPTONES. By P. A. Kober and K. Sugiura 383
A STUDY OF THE CONDUCTIVITY AND DISSOCIATION OF CERTAIN ORGANIC ACIDS IN AQUEOUS SOLUTION AT DIFFERENT TEMPERATURES. By A. Springer, Jr., and Harry C. Jones . . . 411
SOLUBILITY AND DISTRIBUTION COEFFICIENTS OF THYMOL. By Atherton Seidell 453

REVIEWS

Experiments in Organic Chemistry 467
Tables Annuelles Internationales de Constantes et Données Numériques de Chimie, de Physique, et de Technologie . . . 467
The Analyst's Laboratory Companion 468
An Introduction to Quantitative Analysis 469
Methods for Sugar Analysis and Allied Determinations . . . 469
Kolloidchemie 470
Chemical Works 470
Das Erdöl, seine Physik, Chemie, Geologie, Technologie und sein Wirtschaftsbetrieb 472

No. 6

CONTRIBUTIONS FROM THE CHEMICAL LABORATORY OF CORNELL UNIVERSITY:
  Octochloroindigo and Some Derivatives of Tetrachloroanthranilic and Tetrachlorophthalic Acids. By W. R. Orndorff and E. H. Nichols 473
THE CONDUCTIVITY, TEMPERATURE COEFFICIENTS OF CONDUCTIVITY AND DISSOCIATION OF CERTAIN ELECTROLYTES IN AQUEOUS SOLUTIONS AT 35°, 50° AND 65°. By S. F. Howard and Harry C. Jones 500

REPORT

The Molecular Theory 536

OBITUARY

Morris Loeb 547

REVIEWS

Conférences sur quelques Thèmes Choisis de la Chimie Pure et Appliquée 548
Theoretical and Physical Chemistry 548
Spectroscopy 549
Über neue thermodynamische Theorien 551
Die Entdeckung des Radiums 551
Tafeln zum Gebrauche bei der Bestimmung von Brechungsindices . 551
Higher Mathematics for Chemical Students 552
A Concise History of Chemistry 552
The Chemical Constitution of the Proteins 553
The Physiology of Protein Metabolism 553
Annual Tables of Constants 554
Index 555
Errata 575

VOL. XLVIII JULY, 1912 No. 1

AMERICAN CHEMICAL JOURNAL

[Contribution from the Chemical Laboratory of the University of Cincinnati]

THE BECKMANN REARRANGEMENT OF HYDROXAMIC ACIDS

BY LAUDER WILLIAM JONES

I. A SINGULAR CASE OF SPONTANEOUS BECKMANN REARRANGEMENT

II. THE MECHANISM OF THE BECKMANN REARRANGEMENT, AND ITS APPLICATION TO HYDROXAMIC ACIDS

I

It is a well known fact that the hydroxamic acids and many of their derivatives are peculiarly susceptible to rearrangements of the Beckmann type. The early investigations of Lossen[1] and his students furnished many striking illustrations of such rearrangements among hydroxamic acids of the aromatic series.

Lossen observed that mono-, di-, and triacylated derivatives of hydroxylamine, upon distillation, all gave rise to isocyanates or their decomposition products, a change which plainly pointed to reactions of the Beckmann type. Thus he[2] found that a monohydroxamic acid decomposed chiefly in accordance with the following equation:

$$R.C(:O)NHOH = R.N:C:O + H_2O = R.NH_2 + CO_2$$

---

[1] Lossen: Ann. Chem. (Liebig), **161**, 347; **175**, 257; **186**, 1; **252**, 170.

[2] Lossen: *Ibid.*, **175**, 320.

The barium salts,[1] which decomposed even more readily than the monohydroxamic acids themselves, gave aniline, barium carbonate and carbon dioxide. Dihydroxamic acids[2] gave an isocyanate, an acid, an anilide and carbon dioxide:

$$\begin{aligned}&\text{I. } R.C(:O)NHOCOR' = R.N:C:O + HO.CO.R'\\ &\text{II. } R.C(:O)NHOCOR' = RNH.CO.R' + CO_2\end{aligned}$$

The anilide always contained the acid radical which had replaced the hydrogen of the oxime group and the alcohol radical from the other acyl group.

Very interesting results were obtained when the distillation products of triacylhydroxylamines with one anisyl and two benzoyl groups were studied. In terms of the symbols which Lossen[3] employed to designate these compounds, and at the same time to show the order in which the acyl groups successively replaced the hydrogen of hydroxylamine, the three structure isomers with two benzoyl and one anisyl groups were represented as follows (B = benzoyl; A = anisyl):

1. Benzanisbenzhydroxylamine, N.B.A.B.O.
2. Dibenzanishydroxylamine, N.B.B.A.O.
3. Anisdibenzhydroxylamine, N.A.B.B.O.

Upon distillation,[4] these three isomers all gave the same products, but with great variation in the relative proportion of each product:

$$N\left\{\begin{array}{l}COC_6H_5\\ COC_6H_5\\ COC_6H_4OCH_3\end{array}\right\}O = \begin{array}{l}\text{I. } C_6H_5N:C:O + \\ \qquad\qquad C_6H_5CO.O.COC_6H_4OCH_3\\ \text{II. } CH_3OC_6H_4N:C:O + (C_6H_5CO)_2O\end{array}$$

Lossen[5] showed that the two isomers N.B.A.B.O and N.B.B.A.O gave almost exclusively (90 per cent.) products designated by I in the equation above; while the isomer N.A.B.B.O[6] was decomposed chiefly (75 per cent.) according to II. Later in this article, I shall have occasion to discuss this peculiar behavior from the standpoint of the Beckmann rearrangement.

Furthermore, Lossen and Rothmund[7] showed that potassium salts of dihydroxamic acids dissolved in boiling water furnished products which can now be accounted for best by assuming a preliminary Beckmann rearrangement. Thus, the potassium salt of the benzoyl ester of benzhydroxamic acid (dibenzhydroxamic acid of Lossen) gave symmetrical diphenylurea, potassium benzoate and carbon dioxide:

---

[1] Ann. Chem. (Liebig), **186**, 2 (1877).

[2] Pieschel: *Ibid.*, **175**, 305.

[3] *Ibid.*, **175**, 323.

[4] *Ibid.*, p. 44.

[5] *Ibid.*, p. 21.

[6] *Ibid.*, p. 27.

[7] *Ibid.*, **161**, 359; **175**, 257 (1874).

$$2C_6H_5C(OK) : NOCOC_6H_5 + H_2O = (C_6H_5NH)_2C : O + KOOCC_6H_5 + CO_2$$

Somewhat later, Thiele and Pickard[1] studied the rearrangement of several dihydroxamic acids and their potassium salts. They made it evident that even in the case of the salts of these acids it is necessary to assume that, in the reaction with water, the final stage must be preceded by a dissociation of the salt into an isocyanate and a potassium salt of the acid related to the acyl group which had replaced the hydrogen of the oxime group:

$$R.C(OK) : NOCOR' = R.N : C : O + KOOC.R'$$

This isocyanate, in the presence of water, would be hydrolyzed, and the amine thus formed would interact subsequently with a second molecule of isocyanate to give a symmetrical disubstituted urea and carbon dioxide:

$$2R.N : C : O + H_2O = (RNH)_2C : O + CO_2$$

They concluded that such a mechanism might be assumed since, with alcohol in place of water, urethanes frequently were formed instead of disubstituted ureas; while in the presence of strong aqueous ammonia, monosubstituted ureas were produced. These compounds would arise naturally by the addition of alcohol or of ammonia to the isocyanate. In this connection it is interesting to note that Stieglitz and Lengfeldt[2] observed that bromoamides, when treated with sodium methylate, gave urethanes.

Phenylacethydroxamic Acid and its Esters.—Among other hydroxamic acids, Thiele and Pickard[3] prepared and investigated phenylacethydroxamic acid (I) and its acetyl ester (II):

---

[1] Thiele and Pickard: Ann. Chem. (Liebig), **309,** 189 (1899).

[2] Stieglitz and Lengfeldt: This Journal, **15,** 215, 504 (1893).

[3] *Loc. cit.*

$$\underset{\text{I.}}{C_6H_5CH_2C(:O)NHOH} \qquad \underset{\text{II.}}{C_6H_5CH_2C(:O)NHO.CO.CH_3}$$

At the time their results were printed, I was engaged in the preparation of certain hydroxamic acids, among them phenylacethydroxamic acid. Upon the appearance of their article, my work was abandoned. There was, however, one new and particularly interesting observation which I made at that time with the potassium salt of the benzoyl ester of phenylacethydroxamic acid, viz., that in the solid state, at 25°, it spontaneously suffered decomposition and Beckmann rearrangement.[1]

Phenylacethydroxamic acid may be prepared readily in a high state of purity by the action of an alcoholic solution of ethyl phenylacetate upon free hydroxylamine, also dissolved in alcohol. In the course of a few hours the hydroxamic acid separated in large crystals, easily purified by recrystallization from warm ethyl acetate. By the method of Schotten-Baumann, the benzoyl ester of this acid,

$$C_6H_5CH_2C(:O)NHOCOC_6H_5$$

was made. When an alcoholic solution of this ester was treated with the calculated quantity of potassium hydroxide dissolved in alcohol, and sufficient absolute ether was added, a crystalline potassium salt was obtained. This salt, collected rapidly upon a filter, was washed with absolute ether and dried. In the course of a few minutes a dense cloud of white vapor appeared, which sometimes arose with such suddenness that a large vortex ring was sent forth. This vapor consisted entirely of particles of benzyl isocyanate,

$$C_6H_5.CH_2.N:C:O$$

The solid residue which remained scattered upon the support was practically pure potassium benzoate, with a little adhering isocyanate. Even when precautions were taken to exclude moisture during the preparation of the salt, a decomposition occurred after the same manner. When one-half gram samples were used, the time intervening between the separation of the salt from ether and alcohol and its decomposition was quite uniform with different samples, and approximated five minutes at ordinary room temperature (25°). These observations clearly indicated a spontaneous decomposition accompanied by Beckmann rearrangement:

---

[1] Stieglitz: This Journal, **29**, 50 (1903). On the Beckmann Rearrangement. Decennial Publication, University of Chicago, p. 40 (1903).

$$C_6H_5CH_2C(OK) : NOCOC_6H_5 = C_6H_5CH_2N : C : O + KOOCC_6H_5$$

There are cases on record in which the Beckmann rearrangement of compounds in solution is known to occur with readiness, even at moderately low temperatures. Thus, McCoy and Stieglitz[1] observed that dibromosalicylic bromoamide, with the exceedingly negative radical, $C_6H_2Br_2(OH)$, suffered rearrangement below 5° "in the course of a few seconds, and so rapidly that the bromoamide itself could not be isolated." Van Dam[2] noticed that the same change occurred even at —12°. The azides studied by Curtius[3] were found to undergo the Beckmann rearrangement by loss of nitrogen. Recently, G. Schroeter[4] showed that certain azides (e. g., benzazide and *o*-nitrobenzazide), dissolved in benzene at temperatures ranging from 50°–70°, evolved nitrogen when a stream of carbon dioxide was passed through their solutions; isocyanates in almost quantitative amounts were formed. In the case of the salt under consideration, however, a solid at comparatively low temperature, and in the absence of any solvent or reagent commonly employed to effect rearrangement, gave rise to the usual products of such dissociation.

In a similar manner, certain other salts of hydroxamic acids and of some bromoamides, when heated to temperatures considerably above room temperature, have been observed to decompose explosively. There is not sufficient experimental material at hand to admit of speculation at the present time, but it will be interesting to learn what there is in the nature of this particular compound which makes it so sensitive to rearrangement, while other compounds with similar constitutional formulae appear to be markedly more stable. Thus, the sodium salt of the benzoyl ester of phenylacethydroxamic acid does not decompose suddenly, but changes very slowly in the course of many days. Even after several hours the potassium salt of the acetyl ester of phenylacethydroxamic acid showed no tendency to decompose at 25°. At 50°, however, it puffed suddenly after four or five minutes.

---

[1] McCoy and Stieglitz: This Journal, **21,** 116 (1899).

[2] Van Dam: Rec. trav. chim., **18,** 108 (1899); **19,** 318 (1900).

[3] Curtius: J. prakt. Chem., **63,** 428 (1901). Ber. d. chem. Ges., **35,** 3229 (1902).

[4] Schroeter: Ber. d. chem. Ges., **42,** 2336 (1911).

EXPERIMENTAL PART

Phenylacethydroxamic Acid

By the action of hydrogen sulphide upon the copper salt suspended in dry alcohol and ether, Thiele and Pickard[1] obtained phenylacethydroxamic acid, which they describe as a solid melting at 121°. I have found it preferable to prepare the acid by causing ethyl phenylacetate to react with free hydroxylamine.

Forty grams of ethyl phenylacetate were mixed with ten grams of hydroxylamine and enough ethyl alcohol to yield a homogeneous solution. In the course of a few hours, a sample of the solution gave a decided color test with ferric cloride, showing the presence of hydroxamic acid, but it required about four days to complete the reaction. During this time, phenylacethydroxamic acid crystallized from the solution in coarse needles or sometimes in large transparent plates. After the separation of the crystals, the mother liquid was evaporated and yielded more of the acid. In all, about 35 grams were obtained.

Warm ethyl acetate was found to be the best solvent, and was employed in purifying the acid. It could also be crystallized from a solution in boiling water. It was soluble in warm alcohol, but only sparingly soluble in ether or in ligroin. The melting point was found to be 145°–145°.5 with some decomposition.[2].

---

[1] Thiele and Pickard: Ann. Chem. (Liebig), **309,** 201 (1899).

[2] Thiele and Pickard (*loc. cit.*) recorded the melting point as 121°. I have never obtained a sample of the acid which melted at 121°. I was at first inclined to think that the melting point given by Thiele and Pickard might be a misprint; but the fact

An analysis of the acid melting at 145°–145°.5 gave the following values:

0.1814 gram substance gave 15.4 cc. N at 24° and 740.8 mm.

0.1214 gram substance gave 0.2836 gram CO_2 and 0.0675 gram H_2O.

	Calculated for $C_8H_9O_2N$	Found
C	63.58	63.71
H	5.96	6.17
N	9.27	9.33

The Benzoyl Ester of Phenylacethydroxamic Acid $C_6H_5CH_2CONH(OCOC_6H_5)$

The benzoyl ester was made either by fusing the hydroxamic acid with benzoic anhydride (1), or by the Schotten-Baumann method (2).

Method (*1*).—Eight grams of phenylacethydroxamic acid, mixed with a slight excess of benzoic anhydride, were fused at 120° until a sample of the product, when dissolved in water, gave no color test with ferric chloride. After the crude product had been broken up and extracted repeatedly with ligroin to remove benzoic acid and any unchanged benzoic anhydride, the remaining solid was dissolved in boiling alcohol, and hot water was added until the solution became slightly turbid. This solution, upon cooling, deposited brilliant colorless needles of the ester.

Method (*2*).—When the Schotten-Baumann method was employed, the ester was made as follows: Ten and one-half grams of the acid were dissolved in 100 cc. of water and 4 grams of potassium hydroxide were added. Considerable heat was evolved, and after a few minutes a dense precipitate separated. The shaking of the mixture was continued until the odor of benzoyl chloride had practically disappeared. The crude product was then collected, dried, extracted with ligroin, and recrystallized in the manner described above.

that the acetyl ester prepared by Thiele and Pickard melted at 121°, while the acetyl ester which I have made repeatedly melted at 148°–149° would lead to the conclusion that two distinct isomeric phenylacethydroxamic acids have been under investigation in the two instances.

The benzoyl ester melted at 120°.5–121°.5 with indications of fusion at 118°. When it was heated to a temperature slightly above its melting point, the odor of isocyanate became distinctly noticeable at once. The ester was almost insoluble in water and in ligroin. It was only sparingly soluble in ether, but quite readily in warm alcohol.

An analysis gave the following value for nitrogen:

0.338 gram substance gave 16.75 cc. N at 14° and 738.2 mm.

	Calculated for $C_{15}H_{13}O_3N$	Found
N	5.49	5.67

Potassium Salt.—Two grams of the benzoyl ester were dissolved in alcohol and a solution of 0.45 gram of potassium hydroxide was added. The mixture became warm, but no precipitate was formed until ether was added, which caused the tardy separation of a white crystalline salt, heavy and granular in appearance.

This salt was collected upon a filter, and after it had been washed rapidly with ether it was placed upon a porous support to dry. In the course of several minutes, sudden decomposition occurred, in all cases accompanied by a hissing sound and a dense cloud of the vapor of benzyl isocyanate; potassium benzoate remained as a solid residue. The identity of the isocyanate was established by passing the vapor into water, with which it reacted to give symmetrical dibenzylurea,

$$(C_6H_5CH_2.NH)_2CO$$

a solid melting at 169°, identical with a sample of symmetrical dibenzylurea made for comparison. When the solid residue left by the decomposition was dissolved in water, a slight amount of symmetrical dibenzylurea, caused by adhering isocyanate, separated and was removed. Dilute hydrochloric acid added to the filtrate gave crystals of benzoic acid which melted at 121°.

To make sure that the decomposition was not caused by moisture absorbed from the air, precautions were taken to prepare the salt in such a way that moisture was excluded as thoroughly as possible. The salt was collected upon a filter placed under a bell jar through which dry air was passing, and was transferred at once to a desiccator. In the course of five or six minutes, decomposition ensued as before; the force of the decomposition was sufficient to lift the cover of the desiccator and throw it upon the table.

At 0° the salt was comparatively stable. A sample was kept for several hours in a tube surrounded by ice. When, however, it was transferred to a crucible for weighing, it decomposed suddenly before the weighing could be completed.

When the salt, immediately after preparation, was dissolved in cold water, a clear solution was obtained. But if a minute or two had elapsed before the salt was treated with water, a turbid solution invariably resulted. When the clear solution was boiled, a dense crystalline precipitate quickly separated. This was shown to be symmetrical dibenzylurea; it melted at 169°.

An analysis of the potassium salt gave the following value for potassium:

0.5143 gram substance gave 0.1515 gram K_2SO_4.

	Calculated for $C_{15}H_{12}O_3NK$	Found
K	13.33	13.21

Sodium Salt.—The calculated amount of sodium hydroxide dissolved in alcohol was added to an alcoholic solution of the benzoyl ester. The bulky, gelatinous precipitate thrown out by ether was collected and washed with ether. At ordinary room temperature the salt, even after two hours, showed no indications of decomposition; there was no noticeable odor of isocyanate, and the salt gave a clear solution in cold water. When the salt was heated, it puffed and gave benzyl isocyanate.

Analysis:

0.2639 gram substance gave 0.0674 gram Na_2SO_4.

	Calculated for $C_{15}H_{12}O_3NNa$	Found
Na	8.30	8.27

Silver Salt.—By the action of silver nitrate upon a fresh solution of the potassium or the sodium salt, a white precipitate was formed. The silver salt was apparently more stable than either of the other salts. When it was heated on a spatula over the flame it decomposed. A small sample (0.1 gram) in a test tube finally puffed after it had been heated for several minutes at a temperature of 70°.

Acetyl Ester of Phenylacethydroxamic Acid

$C_6H_5.CH_2CO.NH(O.COCH_3)$

Five grams of phenylacethydroxamic acid (melting at 145°–145°.5) were heated with an equal weight of acetic anhydride until a sample of the mixture, when dissolved in water, showed no color reaction with ferric chloride. Considerable heat was evolved during the reaction, and the mixture solidified partially upon cooling. After the product had been dried, it was recrystallized from warm ethyl acetate, from which it separated in long flat crystals which melted at 148°–149°. The ester may be crystallized from alcohol. It is almost insoluble in water and in ligroin, and only sparingly soluble in boiling ether.

Analysis:

0.3279 gram substance gave 22.3 cc. N at 29° and 743.3 mm.

	Calculated for $C_{10}H_{11}O_3N$	Found
N	7.25	7.28

Potassium Salt.—One gram of the acetyl ester was dissolved in alcohol and mixed with an alcoholic solution of potassium hydroxide (1 molecule), but the solution remained clear until ether was added. This caused the salt to separate as a voluminous white precipitate. The salt was washed with ether and dried in a desiccator. It showed no inclination to decompose after the fashion of the potassium salt of the benzoyl ester. However, when a sample (0.1 gram) placed in a test tube was heated in a bath to 70°, it puffed in about two minutes; at 50°, the time required was about six minutes. At room temperature (25°) after two hours there was no visible sign of change; the salt was still completely soluble in water and possessed no odor of isocyanate.

When a water solution of the salt was boiled, symmetrical dibenzylurea was formed, but somewhat more slowly than with the potassium salt of the benzoyl ester. A white silver salt was precipitated upon the addition of silver nitrate to a solution of the sodium salt.

Other Esters of Phenylacethydroxamic Acid

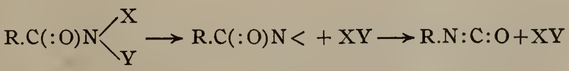
By the action of various acid anhydrides upon phenylacethydroxamic acid, the following esters were prepared: propionyl ester, melting at 138°–139°; normal butyryl ester, melting at 113°–114°; isobutyryl ester, melting at 111°–112°.

II

A. Mechanism of the Beckmann Rearrangement

Since the announcement by Beckmann[1] in 1886 of the singular rearrangement of certain oximes in the presence of phosphorus pentachloride, there has been, perhaps, no other one class of rearrangements among organic compounds which has led to so much investigation. Still, at the present time, it can hardly be said that chemists have reached any unanimity concerning appropriate symbols by which to portray the mechanism of this rearrangement.

The evidence, as I view it, seems to favor the position held by Stieglitz,[2] viz., that the prime factor leading to such rearrangement consists in a dissociation accompanied by a change in valence of the nitrogen atom from three to one, with subsequent readjustment of the groups induced by the presence of univalent nitrogen:



$$\mathrm{R.C(:O)N}\left\langle\begin{matrix}\mathrm{X}\\ \mathrm{Y}\end{matrix}\right. \longrightarrow \mathrm{R.C(:O)N}< + \mathrm{XY} \longrightarrow \mathrm{R.N:C:O} + \mathrm{XY}$$

Evidence has accumulated to establish the fact that the Beckmann rearrangement occurs readily when conditions arise which make it possible by an inspection of the constitutional formulas of certain classes of compounds to predict for nitrogen a change of valence of this kind. Furthermore, rearrangement fails to take place when such conditions are not apparent, or easily realizable by the assumption of plausible intermediate reactions with reagents employed to bring about rearrangement.

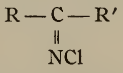
---

[1] Beckmann: Ber. d. chem. Ges., **19**, 988 (1886); **20**, 1507, 2508 (1887). Hofmann: *Ibid.*, **14**, 2725 (1882); **16**, 408 (1883).

[2] J. Stieglitz: This Journal, **18**, 751 (1896); **29**, 49 (1903). Stieglitz and Earl: *Ibid.*, **30**, 399, 412 (1903). Stieglitz and Slosson: Ber. d. chem. Ges., **28**, 3266 (1896) **34**, 1613 (1902). Slossen: This Journal, **29**, 289 (1903).

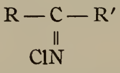
Among the many convincing arguments brought forward by Stieglitz in support of his interpretation, the following may be mentioned as probably of the most weight:

(1) Stieglitz[1] has shown that certain stereoisomeric (*syn* and *anti*) halogen imido esters do not undergo the Beckmann rearrangement even when heated to 140°. This fact leads to the conclusion that the presence of doubly bound nitrogen cannot be the determining factor, or at least not the only determining factor in these rearrangements, as Hantzsch[2] and others would have us believe. Recently, Stieglitz and Peterson[3] have isolated stereoisomeric chlorimido ketones,



$$\begin{array}{c}\mathrm{R-C-R'}\\ \| \\ \mathrm{NCl}\end{array}$$

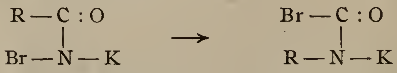
and



$$\begin{array}{c}\mathrm{R-C-R'}\\ \| \\ \mathrm{ClN}\end{array}$$

They have shown that these compounds do not rearrange even at 100°. This effectually disposes of the assumption that chlorimido ketones are the intermediate products in the rearrangement of ketoximes. Such an assumption was made by Hantzsch.[4]

(2) According to the theory of Hoogewerff and van Dorp,[5] rearrangement occurs with salts of bromoamides by virtue of the tendency of nitrogen to combine with radicals more positive than the halogens:



$$\begin{array}{c}\mathrm{R-C:O}\\ | \\ \mathrm{Br-N-K}\end{array} \longrightarrow \begin{array}{c}\mathrm{Br-C:O}\\ | \\ \mathrm{R-N-K}\end{array}$$

Contrary to this assumption, however, it has been shown that of two bromoamides the salt of the one with the more negative group often shows rearrangement with the greater readiness. This is illustrated in a striking manner by the behavior of the bromoamide of dibromosalicylic acid mentioned on page 5. Then again, β-phenyl-β-benzoylhydroxylamine,[1]

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[1] Stieglitz: This Journal, **40**, 36 (1908). Hilpert: *Ibid.*, **40**, 155 (1908).

[2] Hantzsch: Ber. d. chem. Ges., **35**, 3579 (1902).

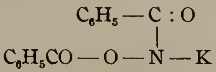
[3] *Ibid.*, **43**, 782 (1900).

[4] *Ibid.*, **24**, 3516 (1891).

[5] Hoogewerff and van Dorp: Rec. trav. chim., **6**, 373 (1887); **8**, 173 (1889), etc.

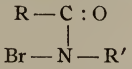
$$C_6H_5N(COC_6H_5)OH$$

under the influence of reagents usually employed to bring about rearrangement, does not give rise to any product of that character; not a trace of diphenylamine could be detected, "and yet the color tests for this substance belong to the most sensitive known to organic chemistry."[2] It is interesting in this connection to consider the behavior of the potassium salt of the benzoyl ester of benzhydroxamic acid, which easily undergoes rearrangement:



$$\begin{array}{r} C_6H_5-C:O \\ | \\ C_6H_5CO-O-N-K \end{array}$$

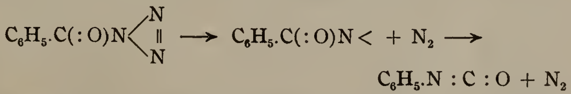
Furthermore, it has been shown that bromoalkylamides,



$$\begin{array}{c} R-C:O \\ | \\ Br-N-R' \end{array}$$

do not rearrange,[3] although, on the assumption of Hoogewerff and van Dorp there is no apparent reason why such compounds should not do so.

(3) The interpretation offered by Stieglitz is the only one which, in an unconstrained way, can explain the decomposition and rearrangement of azides and diazides:[4]



$$C_6H_5.C(:O)N\Big\langle\begin{array}{c} N \\ \| \\ N \end{array} \longrightarrow C_6H_5.C(:O)N< + N_2 \longrightarrow C_6H_5.N:C:O + N_2$$

(4) Perhaps the most convincing argument is to be found in the behavior of triphenylmethylhydroxylamine, which has been shown by Stieglitz[5] to suffer the Beckmann rearrangement when the usual reagents are allowed to act upon it:

$$(C_6H_5)_3C.NHOH \longrightarrow (C_6H_5)_3C.N< + H_2O \longrightarrow (C_6H_5)_2C:NC_6H_5 + H_2O$$

---

[1] Stieglitz: This Journal, **29**, 53 (1903).

[2] *Ibid.*, **29**, 53 (1903).

[3] *Ibid.*, **29**, 289 (1903).

[4] Curtius: *Loc. cit.* Schroeter: Ber. d. chem. Ges., **44**, 1207 (1911).

[5] Stieglitz: *Ibid.*, **46**, 327 (1911), note.

Benzophenone phenylimide was formed, and its presence was established by hydrolysis; it gave benzophenone and aniline.

Unless we wish to claim that in the final analysis the different classes of compounds which show molecular rearrangements up to this time regarded as belonging to the Beckmann type may yield similar products by reactions essentially different in kind, it would seem to me that the evidence presented above is convincing enough to force upon us the conclusion of Stieglitz, that the predisposing cause is to be sought in the potency of the free valences of *univalent nitrogen*; at least, this hypothesis has offered a mechanism which explains most of the known facts, and does so in a manner less constrained than any other proposed interpretation has yet succeeded in doing.

B. Application to Hydroxamic Acids

Amides.—In applying this viewpoint to the rearrangement of hydroxamic acids, certain characteristic properties of the amides may be considered first, since our present modes of formulating the reaction of the hydroxamic acids are largely based upon analogies drawn from these compounds.

In the case of amides and monohalogen amides, many investigations, chemical as well as physical-chemical in character, have shown that they are unquestionably tautomeric in chemical behavior. In no single instance, however, have chemists succeeded in isolating the two isomeric amides which structure chemistry predicts. Hantzsch[1] pointed out that neither the amides nor their salts will give color reactions with ferric chloride, and that they do not react with phenyl isocyanate. On the other hand, Buehner[2] showed that, by the action of dimethyl sulphate, some amides can be converted into imido esters. Thus, benzamide was changed into the methyl sulphate derivative of its methyl imido ester to the extent of 90 per cent. Similar results have been obtained with diazomethane. Hantzsch and Dollfus[3] concluded that the halogen amides, R.CO.NH(Hal), were to be regarded as pseudo acids because of their behavior with ammonia in various organic solvents (Hantzsch's "ammonia reaction" for pseudo acids). This method,[1] however, has lost much of the certainty ascribed to it originally.

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[1] Hantzsch: Ann. Chem. (Liebig), **296,** 90 (1897).

[2] Buehner: *Ibid.,* **333,** 289 (1904).

[3] Hantzsch and Dollfus: Ber. d. chem. Ges., **35,** 228, 250 (1902).

Although the salts of amides have been generally assigned imido salt formulas, R.C(OMe) : NH, there is, perhaps, at present more diversity of opinion on this point than ever before. Long ago the inconsistency of assuming that the alkali or the silver salts of such substances as nitrous, sulphurous, hydrocyanic acids, ethyl acetoacetate, etc., were mixtures of two independent isomeric salts in a definite fixed ratio became apparent to all; for the amounts of two isomeric derivatives formed by the interaction of a reagent with any one of these salts was not fixed, but varied with the reagent employed, as well as with the alterable physical conditions of the experiment.

Investigation showed that rearrangements of alkyl and acyl derivatives of these acids frequently occurred under the influence of heat or certain chemical reagents. Thus isonitriles passed into nitriles; symmetrical esters of sulphurous acid into sulphonic acids; esters of thiocyanic acid into mustard oils; O-derivatives of ethyl acetoacetate into C-derivatives. Even in the case of the silver and alkali salts of the amides, at first thought to give oxygen-alkyl or nitrogen-alkyl derivatives, respectively, the experiments of Comstock and Wheeler[2] and later of other investigators tended to confirm the belief that neither the alkali nor the silver salt gave exclusively one type of alkyl isomer, but that, depending upon temperature and the presence of an excess of reagent (e. g., halogen alkyl[3]), the oxygen ester first formed seemed to suffer rearrangement to give the nitrogen-alkyl isomer. So that, notwithstanding the simultaneous formation of two isomers, the belief remained practically unshaken that all of the salts of amides were to be represented by formulas with the metal bound to oxygen.

On the other hand, there appeared to be evidence, fragmentary to be sure, which pointed to the existence of salts which must be represented by formulas in which the metal was bound to nitrogen. Thus, Ley and Kissel[1] inferred from the electrical conductivity and chemical behavior of mercury acetamide that it more probably should be represented by the amide formula, $Hg(NH.CO.CH_3)_2$. Schroeter[2] is inclined to represent bromoamide salts by formulas with sodium bound to nitrogen, R.CO(NBrNa). He assumed that the decomposition of these salts, with loss of sodium bromide and rearrangement, would be more satisfactorily pictured by this formula in terms of the views which Stieglitz holds concerning the Beckmann rearrangement. By the action of solutions of mercuric salts upon solutions of trisodium cyanurate at 0° and at 100°, Hantzsch[3] obtained two isomeric mercury salts totally different in chemical behavior. At 0°, a salt which Hantzsch represented by the formula $(CN)_3(OHg)_3.2H_2O$ was obtained. At 100° the isomeric salt $(CO)_3(NHg)_3.H_2O$ resulted. Both salts could be dehydrated without decomposition. These salts would therefore correspond to the amide and the imide salt forms,

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[1] Hantzsch: Ber. d. chem. Ges., **40**, 3804 (1907). Michael: *Ibid.*, 4380, 4916 (1907).

[2] Comstock and Wheeler: This Journal, **13**, 522 (1891).

[3] Wheeler: *Ibid.*, **21**, 185 (1899); **23**, 140 (1901).

$$—C(O\ Hg):N— \qquad —C(:O)N\ Hg—$$

Those who clung to the oxygen theory of the salts were forced to seek some mechanism whereby two isomers might be formed simultaneously or the isomer with the group bound to oxygen might be transformed into the modification with the same group linked to nitrogen. The rearrangement was explained by Wheeler[4] as a process of addition in which the halogen alkyl united with the imido ester in such a way that the alkyl group attached itself to nitrogen and the halogen to carbon. Exception has been taken to this mechanism by Brunel and Acree,[5] who point out that "the fact that rearrangement may take place is no proof that it alone is accountable for the formation of two products." In the alkylation experiments with urazole salts, which they carried out quantitatively under varying conditions, for each salt a mixture of

[1] Ley and Kissel: Ber. d. chem. Ges., **32**, 1358 (1899).
[2] Schroeter: *Ibid.*, **43**, 2337 (1910).
[3] Hantzsch: *Ibid.*, **35**, 2718 (1902).
[4] Wheeler: This Journal, **21**, 187 (1899).
[5] Brunel and Acree: *Ibid.*, **43**, 512 (1910).

oxygen-alkyl and nitrogen-alkyl derivatives was formed in practically constant ratio. If the oxygen ester had rearranged to give the nitrogen ester, the ratio of the amounts of these two esters should have varied with the time of reaction, etc., but no such variation was observed by Brunel and Acree.

Michael[1] and others sought to account for the two forms by assuming that the oxygen ester was produced by the direct replacement of the metal, while the nitrogen derivative was obtained by the addition of the reagent to the double bond between nitrogen and carbon, with subsequent loss of a salt.

Another device, the rearranged anion, has been used by several investigators (Nef, Lapworth, and others)[2] although the scheme tacitly is almost, if not quite, an admission of the existence of salts in tautomeric equilibrium. It at least presupposes the existence of tautomeric anions in equilibrium, and unless the salts to which these anions belong are dissociated to an infinite degree, a certain per cent. of the two corresponding tautomeric salts must be present in the system too.

Acree and his collaborators,[3] in a study of the urazole and thiourazole salts, have not hesitated to assume the existence of tautomeric salt isomers and anions in equilibrium, and have published quantitative results which seem to verify their conclusions. These salts would correspond to the amide and imide forms:

$$—C(:O)NNa— \qquad\qquad —C(ONa):N—$$

It is quite probable that in the future two distinct modifications (salt isomers) of the salts of amides will be isolated; possibly the orange and white silver salts of different stabilities already isolated[4] in certain cases may represent such isomers.

Monohydroxamic Acids.—The monohydroxamic acids present a possibility of tautomerism very similar to that proposed for amides. No agreement concerning the formula of the free hydroxamic acids has yet been reached. Possibly because of the stereoisomeric relations observed in the case of certain esters, $R.C(OR') : NOH$, preference has usually been given to the hydroximic form, $R.C(OH) : NOH$, although no valid experimental objection can be raised against the hydroxamic formula, $R.C(: O)NHOH$. The hydroxamic formula would more naturally express the decomposition according to the view of Stieglitz:

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[1] Michael: J. prakt. Chem., **37**, 469; **45**, 580; **46**, 189, etc. THIS JOURNAL, **43**, 322. Ber. d. chem. Ges., **43**, 621. Nef: Ann. Chem. (Liebig), **266**, 52; **276**, 200; **277**, 59, 83; **298**, 263, etc.

[2] Nef: Ann. Chem. (Liebig), **309**, 157, 158 (1899). Lapworth: J. Chem. Soc., **81**, 1503 (1902); **83**, 1121 (1903); **85**, 30 (1904).

[3] Acree: THIS JOURNAL, **38**, 1; **39**, 125, 226. Ber. d. chem. Ges., **41**, 3199. Nirdlinger and Acree: THIS JOURNAL, **43**, 358 (1910). Brunel and Acree: *Ibid.*, **43**, 517 (1910).

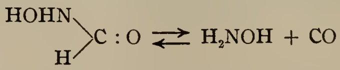
[4] Titherley: J. Chem. Soc., **71**, 466 (1898); **79**, 408 (1901).

$$RC(: O)NHOH \longrightarrow R.C(: O)N< + H_2O \longrightarrow$$
$$R.N : C : O + H_2O \longrightarrow RNH_2 + CO_2$$

In the case of formhydroxamic acid, at least, the hydroxamic formula is the more plausible by far, since it accounts for the fact that formhydroxamic acid and its salts do not yield fulminic acid or fulminates,[1] as they would be expected to do very readily if the hydroximic formula were chosen for them:

$$HOHC : NOH \longrightarrow HOH + >C : NOH$$

Instead of these products, formhydroxamic acid, upon dissociation, readily gives carbon monoxide and hydroxylamine,[2] a reaction which was found by me to be slightly reversible:[3]



$$\begin{matrix} HOHN \diagdown \\ H \diagup \end{matrix} C : O \rightleftarrows H_2NOH + CO$$

Furthermore, in the presence of alkalies it undergoes the Beckmann rearrangement, and yields carbonates and ammonia:[4]

$$H.C(: O)NHOH \longrightarrow H.C(: O)N< + H_2O \longrightarrow$$
$$H.N : C : O + H_2O \longrightarrow NH_3 + CO_2$$

The Dihydroxamic Acids.—The acyl esters of monohydroxamic acids (dihydroxamic acids) have been regarded as tautomeric in behavior and, so far as evidence goes, may be represented by the two formulas:

$$RC(: O)NHOCOR' \qquad RC(OH) : NOCOR'$$

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[1] Jones: This Journal, **20**, 27–32 (1898). Biddel: Ann. Chem. (Liebig), **310**, 13 (1900).

[2] Jones, Biddell: *Loc. cit.*

[3] Jones and Oesper: This Journal, **42**, 516 (1909).

[4] Wieland: Die Knallsäure, p. 32 (1909).

The former would lend itself to an interpretation of the rearrangement in accordance with the theory of Stieglitz, and would thus explain the ease with which a dihydroxamic acid upon distillation gives a fatty acid, an isocyanate, an anilide and carbon dioxide:

$$\mathrm{R.C(:O)NHOCOR'} \longrightarrow \mathrm{R.C(:O)N{<}} + \mathrm{HOOC.R'} \longrightarrow \mathrm{R.N:C:O} + \mathrm{HOOC.R'}$$

Of course, if the hydroximic formula is considered, it will be apparent that there would be no inconsistency in assuming a loss of acid, HOC(: O)R.

The Salts of Dihydroxamic Acids.—Similar to the salts of bromoamides, these salts have usually been represented by hydroximic formulas:

R.C(OMe) : NOCOR′	R.C(: O)NMe.OCOR′
Hydroximic Formula	Hydroxamic Formula

Schroeter[1] has ventured to propose that the metal might be linked to nitrogen, and has suggested that this formula would lend itself more readily to the interpretation of the rearrangement of these salts in accordance with Stieglitz's view of the Beckmann rearrangement.

Evidence of the existence of tautomeric salt isomers among these salts is suggested by experiments which I carried out in 1897.[2] By the action of benzoyl chloride upon the sodium salt of the benzoyl ester of acethydroxamic acid,

$$\mathrm{CH_3C(:O)NNa.OCOC_6H_5}$$

two compounds were formed: a solid melting at 68–69°, and an oil. This solid was shown to be α-benzoyl-β-acetylbenzoylhydroxylamine, a real triacylated hydroxylamine,[3]

$$\mathrm{CH_3C(:O)N(COC_6H_5)OCOC_6H_5}$$

The sufficiency of this formula was established by two methods. In the first place, upon alcoholysis[4] with alcoholic potash the solid (melting at 68°–69°) gave exclusively the

[1] Schroeter: Ber. d. chem. Ges., **44,** 1201 (1911).

[2] Jones: This Journal, **20,** 13 (1898).

[3] Jones: *Loc. cit.*, p. 15.

[4] *Loc. cit.*, p. 15.

benzoyl ester of benzhydroxamic acid (dibenzhydroxamic acid),

$$C_6H_5C(:O)NH(OCOC_6H_5)$$

and ethyl acetate. *Not a trace of the benzoyl ester of acethydroxamic acid,*

$$CH_3.C(:O)NH(OCOC_6H_5)$$

could be found. The oil[1] which accompanied this solid was hydrolyzed and gave the benzoyl ester of acethydroxamic acid and ethyl benzoate almost exclusively. This oil, therefore, consisted almost entirely of the O-isomer, the benzoyl ester of benzoylacethydroximic acid,

$$CH_3C(OCOC_6H_5):NOCOC_6H_5$$

In the second place, the same solid compound (melting at 68°–69°) was made by the action of acetyl chloride upon the potassium salt of the benzoyl ester of benzhydroxamic acid,

$$C_6H_5C(:O)NK—OCOC_6H_5$$

The identity[2] of the two substances was established by the fact that both gave the same products upon alcoholysis, by a crystallographic comparison of the crystals, and by the constancy of the melting point of a mixture of crystals prepared in the two ways. An O-isomer formed in this second reaction,

$$C_6H_5C(OCOCH_3):NOCOC_6H_5$$

was a solid melting at 84°–85°. Upon alcoholysis it gave the benzoyl ester of benzhydroxamic acid and ethyl acetate.

From the standpoint of tautomeric salts, the formation of an identical product in the two cases would be explained by the presence of the two nitrogen salt isomers:

$$\underset{\text{I}}{CH_3C(:O)NK.OCOC_6H_5} \qquad \underset{\text{II}}{C_6H_5C(:O)NK.OCOC_6H_5}$$

The first salt with benzoyl chloride would plainly yield the same compound which the second salt would give when acted upon by acetyl chloride, viz.,

$$CH_3C(:O)N(COC_6H_5).OCOC_6H_5$$

Since these experiments were largely qualitative in character, the proposed interpretation is based chiefly upon analogy, and until quantitative results are obtained it will not be possible to state positively that the reactions could not be accounted for by a rearrangement of the O-acyl to the N-acyl compound, a reaction which seems to play a role in certain reactions of the triacylated hydroxylamines.

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[1] *Loc. cit.*

[2] Jones: *Loc. cit.*

A possible interpretation of the singular behavior of the potassium salt of phenylacethydroxamic acid benzoyl ester described above may be deduced from a tautomeric equilibrium between two salts:

$$C_6H_5CH_2C(OK):NOCOC_6H_5 \rightleftarrows C_6H_5CH_2C(:O)NK.OCOC_6H_5$$

If this reaction is assumed to proceed from left to right with a measurable velocity, and if the form on the right should dissociate into an isocyanate and potassium benzoate, there may be an autocatalytic effect which accelerates the reaction from left to right; or, because of the suppression of the one form by dissociation and Beckmann rearrangement, the reaction, at the proper temperature, of its own accord may proceed with sufficient velocity to permit the heat evolved to more than counterbalance that lost by conduction and otherwise, so that the action may soon reach the violence of an explosion. The phase of the reaction is now being investigated.

Triacyl Derivatives of Hydroxylamine.—The explanation of the products formed by the rearrangement of triacylated hydroxylamines is a much more complicated problem. The conclusions reached in the preceding section of this paper make it evident that each triacylated hydroxylamine may exist in two isomeric structure forms, as well as in several polymorphous modifications.[1]

In proposing a hypothesis to account for the behavior of these compounds it is significant to note that rearrangements among O-acyl compounds have been reported frequently. Thus, Werner and Skiba[2] showed that the benzoyl ester of

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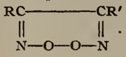
[1] Lossen: *Loc. cit.*

[2] Werner and Skiba: Ber. d. chem. Ges., **27,** 2198 (1894); **32,** 1654 (1899). In most cases two products were formed, viz., the acylhydroxamic acid and a dioximehyperoxide,



$$\begin{array}{ccc} RC & \text{———} & CR' \\ \Vert & & \Vert \\ N-O & & O-N \end{array}.$$

benzhydroximic acid, a solid melting at 95°, could be kept only a short time, since it rapidly rearranged to give dibenzhydroxamic acid:

$$C_6H_5C(OCOC_6H_5) : NOH \longrightarrow C_6H_5C(: O)NHOCOC_6H_5$$

The same tendency to rearrange was manifested by other acyl derivatives, such as the *m*-chlorobenzoyl, *m*-nitrobenzoyl, *p*-nitrobenzoyl esters, etc.; in some cases it was impossible to isolate the acyl hydroximic acid. Similarly, attempts to make acyl imido esters[1] have led invariably to the formation of diamides by rearrangement:

$$RC(OCOR) : NH \longrightarrow RC(: O)NHCOR$$

In the destructive distillation of triacylated hydroxylamines, it would be reasonable to assume that similar rearrangements may occur, and this seems necessary if the products actually formed are to be accounted for. Steiner[2] showed that tribenzoylhydroxylamine upon distillation was almost completely dissociated into phenyl isocyanate and benzoic anhydride. If this triacyl derivative is not a real hydroxylamine but its tautomer, the probability that it will change to the hydroxylamine form upon distillation seems very great. Upon this assumption the following reactions would occur:

$$C_6H_5C(OCOC_6H_5) : NOCOC_6H_5 \longrightarrow$$
$$C_6H_5C(: O)N(COC_6H_5)OCOC_6H_5 \longrightarrow$$
$$C_6H_5C(: O)N< + (C_6H_5.CO)_2O \longrightarrow$$
$$C_6H_5N : C : O + (C_6H_5CO)_2O$$

When, however, the products formed by the distillation of the isomeric hydroxylamine derivatives with two benzoyl and one anisyl group are inspected, it will be clear that even the shifting of the acyl groups from O to N cannot logically account for the fact that, by dissociation and rearrangement, benzanisbenzhydroxylamine (N.B.A.B.O) decomposed to the extent of 10 per cent. into *p*-methoxyphenyl isocyanate and benzoic anhydride. Furthermore, since dibenzanishydroxylamine (N.B.B.A.O) and anisdibenzhydroxylamine (N.A.B.B.O) by a shifting of an acyl group from O to N should yield the same hydroxylamine derivative, viz.,

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[1] Pinner: Ber. d. chem. Ges., **25**, 1434 (1892).

[2] Steiner: Ann. Chem. (Liebig), **178**, 225 (1875).

$$C_6H_5C(:O)N(COC_6H_4OCH_3)OCOC_6H_5$$

it is not plain why the dibenzanishydroxylamine should yield phenyl isocyanate and benzoylanisyl oxide to the extent of 90 per cent. (p. 2), while anisdibenzhydroxylamine should yield only 25 per cent. (p. 2) of the same products.

A possible interpretation of the formation of *p*-methoxyphenyl isocyanate may be found in the following assumption: Upon decomposition benzanisbenzhydroxylamine should undergo the following changes:

$$\begin{aligned}&C_6H_5C(OCOC_6H_5):NOCOC_6H_4OCH_3 \longrightarrow\\ &\quad C_6H_5C(:O)N(COC_6H_5)OCOC_6H_4OCH_3 \longrightarrow\\ &\qquad C_6H_5C(:O)N< + C_6H_5CO.O.COC_6H_4OCH_3 \longrightarrow\\ &\qquad\qquad C_6H_5.N:C:O + C_6H_5CO.O.COC_6H_4OCH_3\end{aligned}$$

It may be assumed that the intermediate product, $C_6H_5CON<$, before rearrangement may interact by addition in two different ways with the recently formed anhydride. In the first place, the original triacylhydroxylamine would be formed; in the second place, an isomer,

$$C_6H_5C(:O)N(COC_6H_4OCH_3)OCOC_6H_5$$

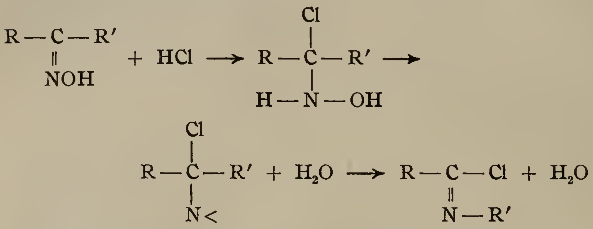
This form, by loss of benzoic anhydride and Beckmann rearrangement, would give *p*-methoxyphenyl isocyanate.

The second difficulty mentioned above furnishes the most serious objection, and so far as I can see no satisfactory explanation of it can be given in the language of the hypothesis. One might imagine that during the process of rearrangement of the O-acyl to the N-acyl derivative, a condition favoring the loss of a particular anhydride (e. g., anisyl benzoyl oxide in the case of dibenzanishydroxylamine), might exist, so that in this instance an excess (90 per cent.) might be found to dissociate into phenyl isocyanate; but this proposal savors too much of calling in the Nascent State to help out.

C. Stereoisomers and the Beckmann Rearrangement

From the standpoint of stereoisomerism the hypothesis of Stieglitz does not seem to form a complete picture of the mechanism of the Beckmann rearrangement, and it is in this field that it has met with the most criticism.[1]

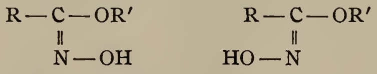
To account for the Beckmann rearrangement of oximes in terms of his hypothesis, Stieglitz[2] was forced to assume the addition of some reagent, HX (e. g., hydrogen chloride), to the double bond between nitrogen and carbon; then the subsequent loss of water would lead to univalent nitrogen and the accompanying rearrangement:



$$\underset{\substack{\| \\ NOH}}{R-C-R'} + HCl \longrightarrow R-\overset{\substack{Cl \\ |}}{\underset{\substack{| \\ H-N-OH}}{C}}-R' \longrightarrow$$

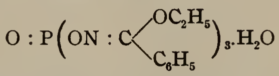
$$R-\overset{\substack{Cl \\ |}}{\underset{\substack{| \\ N<}}{C}}-R' + H_2O \longrightarrow R-\underset{\substack{\| \\ N-R'}}{C}-Cl + H_2O$$

Like the oximes, alkyl esters of hydroximic acids exist in stereoisomeric modifications (*syn* and *anti*):



$$\underset{\substack{\| \\ N-OH}}{R-C-OR'} \qquad \underset{\substack{\| \\ HO-N}}{R-C-OR'}$$

Werner[3] found that with phosphorus pentachloride one of these isomers suffered the Beckmann rearrangement, while the second isomer under similar treatment showed no inclination to take part in such a rearrangement, but gave instead a complex ester of phosphoric acid,



$$O:P\left(ON:C\begin{matrix} \diagup OC_2H_5 \\ \diagdown C_6H_5 \end{matrix}\right)_3.H_2O$$

One cannot avoid surprise that a single isomer and not both should undergo rearrangement, provided the presence of univalent nitrogen alone determines the possibility of such rearrangement, since the addition of hydrogen chloride would be expected to occur equally well in the case of each isomer if stereoisomeric relations exert no modifying influence to prevent it.

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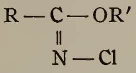
[1] Montagne: Ber. d. chem. Ges., **43**, 2014 (1910).

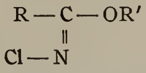
[2] Stieglitz: This Journal, **18**, 751 (1896), note. Stieglitz and Peterson: Ber. d. chem. Ges., **43**, 784 (1910). Schroeter: *Ibid.*, **44**, 1207 (1911). Nef: This Journal, **18**, 753 (1896).

[3] Werner: Ber. d. chem. Ges., **25**, 33 (1892); **26**, 1562 (1893); **29**, 1153 (1896).

Then again, it would seem probable that the stereoisomeric chloroimido esters,



$$\begin{array}{rcl} \mathrm{R}- & \mathrm{C} & -\mathrm{OR'} \\ & \| & \\ & \mathrm{N} & -\mathrm{Cl} \end{array}$$

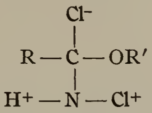


$$\begin{array}{rcl} \mathrm{R}- & \mathrm{C} & -\mathrm{OR'} \\ & \| & \\ \mathrm{Cl}- & \mathrm{N} & \end{array}$$

studied by Stieglitz,[1] might have rearranged, provided this rearrangement may be induced by the addition of hydrogen chloride to the double bond, while, as a matter of fact, a totally different reaction occurred:

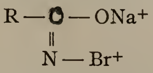
$$\mathrm{R.C(OR)} : \mathrm{NCl} + 2\mathrm{HCl} \longrightarrow \mathrm{R.C(OR)} : \mathrm{NH.HCl} + \mathrm{Cl_2}$$

Of course, in this case, it must be assumed that the specific character of hypochlorous chlorine $(\mathrm{Cl^+})$[2] is the determining factor, and that the addition of hydrochloric acid to the chloroimido ester,



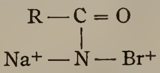
$$\begin{array}{rcl} & \mathrm{Cl^-} & \\ & | & \\ \mathrm{R}- & \mathrm{C} & -\mathrm{OR'} \\ & | & \\ \mathrm{H^+}- & \mathrm{N} & -\mathrm{Cl^+} \end{array}$$

does not necessarily lead to univalent nitrogen by loss of hydrochloric acid since both the hydrogen and the chlorine attached to nitrogen have like sign, viz., (+). Consequently, the loss of chlorine $(\mathrm{Cl^+.Cl^-})$ would seem to be the more probable reaction, and is at any rate the one which actually does occur. In the case of chloroamide or bromoamide salts[3] there is a very singular difference in behavior; in the presence of alkali these salts rearrange with great readiness. An inspection of the formulas will show that, similarly, in this case both the halogen and the sodium must be represented with a + charge.



$$\begin{array}{rcl} \mathrm{R}- & \mathrm{C} & -\mathrm{ONa^+} \\ & \| & \\ & \mathrm{N} & -\mathrm{Br^+} \end{array}$$

or



$$\begin{array}{rcl} \mathrm{R}- & \mathrm{C} & =\mathrm{O} \\ & | & \\ \mathrm{Na^+}- & \mathrm{N} & -\mathrm{Br^+} \end{array}$$

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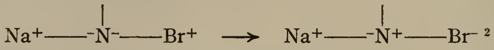
[1] Stieglitz: This Journal, **40**, 40 (1908).

[2] Noyes: J. Am. Chem. Soc., **23**, 463 (1901). Stieglitz: *Ibid.*, **23**, 769 (1901); **29**, 51 (1903). Walden: Z. physik. Chem., **43**, 407–43 (1903). J. J. Thompson: The Corpuscular Theory of Matter, p. 130 (1907). Stieglitz and Peterson: Ber. d chem. Ges., **43**, 782 (1910).

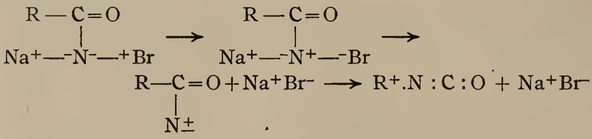
[3] Van Dam: Rec. trav. chim., **18**, 408 (1899).

In terms of the corpuscular atomic hypothesis, before a loss of $Na^{+}Br^{-}$ can occur, there must be an interchange of electrons between the nitrogen and the bromine[1] which may be represented as follows:



$$Na^{+}——{}^{-}\overset{|}{N}{}^{-}——Br^{+} \longrightarrow Na^{+}——{}^{-}\overset{|}{N}{}^{+}——Br^{-}$$ [2]

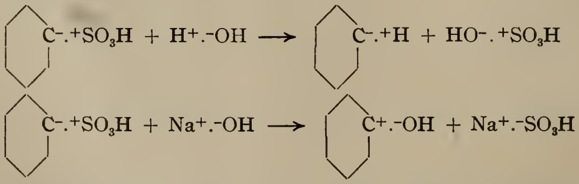
With this transfer accomplished, which amounts to an intramolecular oxidation, the resulting compound would be a salt of the hydrobromic acid ester of a hydroxamic acid, and the loss of $Na^{+}Br^{-}$ would be comparable to the loss of $K^{+}.{}^{-}O.CO.C_6H_5$ from the potassium salt of the benzoyl ester of phenylacethydroxamic acid described above. The complete rearrangement of the bromoamide would be pictured as follows:



$$\begin{array}{c}R—C=O\\ |\\ Na^{+}—{}^{-}N^{-}—{}^{+}Br\end{array} \longrightarrow \begin{array}{c}R—C=O\\ |\\ Na^{+}—{}^{-}N^{+}—{}^{-}Br\end{array} \longrightarrow$$

$$\begin{array}{c}R—C=O\\ |\\ N^{\pm}\end{array} + Na^{+}Br^{-} \longrightarrow R^{+}.N:C:O + Na^{+}Br^{-}$$

Reactions with other classes of organic compounds will be found to require similar assumptions in terms of the corpuscular atomic hypothesis. Thus, benzenesulphonic acid with superheated steam[3] gives benzene and sulphuric acid (comparable to the formation of an amide and hypobromous acid from a bromoamide); but upon fusion with sodium hydroxide it yields phenol and a sulphite.



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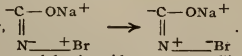
[1] Stieglitz: THIS JOURNAL, **29**, 51 (1903). Stieglitz and Peterson: Ber. d. chem. Ges., **43**, 782 (1910).

[2] Or,



$$\begin{array}{c}-C—ONa^{+}\\ \|\\ N^{-}——{}^{+}Br\end{array} \longrightarrow \begin{array}{c}-C—ONa^{+}\\ \|\\ N^{+}——{}^{-}Br\end{array}.$$

[3] Some sulphonic acids pass so readily into hydrocarbons that thorough mixing with concentrated sulphuric acid in the cold will bring about this change.

In this case the hypothesis requires a transfer of negative electrons from carbon to sulphur. The difficulty would be the same if the sulphonic acid were regarded as a derivative of sulphurous acid, except that the negative electrons would then pass from sulphur to carbon. In a similar manner, hydroxylaminesulphonic acid, $(HO)HNSO_3H$, or its salts, with water and dilute acids decomposed to give hydroxylamine[1] and sulphuric acid. On the other hand, with sodium hydroxide and water, they probably gave dihydroxylamine, $(HO)_2NH$, which subsequently was converted into a salt of hyponitrous acid.[2]

$$\text{I. } HONHSO_3H + H^+.^-OH \longrightarrow HONH_2 + HO^-.^+SO_3H \longrightarrow NH_3(OH)SO_4.$$

$$\text{II. } 2HONHSO_3H + 6Na^+.^-OH \longrightarrow 2HONHOH + 2Na^+.^-SO_3Na + 2NaOH + 2H_2O \longrightarrow Na_2O_2N_2 + 2Na_2SO_3 + 6H_2O$$

If the Beckmann rearrangement depends solely upon the formation of univalent nitrogen, which in the case of oximes[3] must presume the addition of some reagent, HX, to the double bond, it is not plain at first glance why, upon rearrangement, two oximes of different configurations should not yield the same products, or a mixture of products in the same fixed proportion,[4] a conclusion at variance with our usual experience.[5] For if an oxime should combine with a reagent HX by addition, the double bond would disappear from the formula, and the nitrogen would then be linked by a single bond to carbon, a condition which, in terms of the generally accepted hypothesis, would be expected to lead to free rotation, so that the significance of *syn* and *anti* would disappear at once.[1] Schroeter[2] takes exception to this commonly accepted view, and has proposed an hypothesis to avoid it. He assumes that the addition of the reagent HX to the double bond is followed by a subsequent loss of water, hydrogen chloride, etc., to give stereoisomeric univalent nitrogen compounds,

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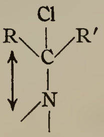
[1] Raschig: Ber. d. chem. Ges., **20**, 584 (1887). Ann. Chem. (Liebig), **241**, 161 (1887).

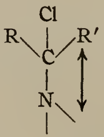
[2] Diver and Haga: J. Chem. Soc., **55**, 750 (1889); **75**, 77 (1899). Z. anorg. Chem., **16**, 428 (1898).

[3] Stieglitz: *Loc. cit.*

[4] Montagne: Ber. d. chem. Ges., **43**, 2015 (1910).

[5] Schroeter (Ber. d. chem. Ges., **44**, 1207 (1911)) has recently shown that some doubt may be attached to our methods of determining the configurations of stereoisomeric oximes. When he treated pivalophenone oxime, $(H_3C)_3CC(C_6H_5) : NOH$, with phosphorus pentachloride, the tertiary butyl group was found to wander to nitrogen, while with acetic acid and hydrochloric acid the phenyl group was the one which shifted.





and that the change in position of the groups R and R′ may take place so rapidly that the effect of free rotation, if it occurs at all, may become negligible. This is plainly a case of begging the question, and does not afford an interpretation, but merely a restatement of the difficulty.

Montagne[3] has called attention to the fact that by the addition of some reagent HX to stereoisomeric oximes, intermediate compounds with asymmetric carbon atoms would result, but that this of itself would not account for the differences in the behavior of the two configurations upon rearrangement, since the two optical isomers obtained from one geometrical isomer must be identical with the two optical isomers obtained from the other geometrical isomer.

When these difficulties are looked at seriously, there appear to be peculiar determining factors not yet included in our explanations, the significance of which Stieglitz[4] has not hesitated to acknowledge in the following statement: "The problem of the influence of stereoisomerism must be subjected to critical experimental investigation."

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[1] Montagne: *Loc. cit.*

[2] *Loc. cit.*

[3] Montagne: Ber. d. chem. Ges., **43**, 2015 (1910).

[4] Stieglitz: This Journal, **18**, 154 (1896), note.

THE OSMOTIC PRESSURE OF CANE SUGAR SOLUTIONS AT HIGH TEMPERATURES[1]

By H. N. Morse, W. W. Holland, C. N. Myers, G. Cash and J. B. Zinn

It was shown in our last paper[2] that between 0° and 25° the osmotic pressures of all concentrations of cane sugar solutions, up to that in which a gram-molecular weight of the substance is dissolved in 1000 grams of water, obey quite exactly the law of Gay-Lussac for gases; in other words, that between these limits of temperature the ratio of osmotic to calculated gas pressure is constant for each concentration of solution. On the other hand, it was not obvious from the pressures obtained between 0° and 25° whether they do, or do not, obey the law of Boyle for gases. The osmotic pressures which were measured were all larger than the corresponding calculated gas pressures of the solute; and, in general, they were not proportional to the supposed concentrations of the solutions. The constancy of the osmotic-gas pressure ratio for each concentration, and the variation in the ratios with changes in concentration, are shown in Table I, which is borrowed from the paper to which reference has been made.

It will be seen that the osmotic pressures exceeded the calculated gas pressures by not less than 6 per cent. (0.2, 0.3 and 0.4 weight-normal solutions), and that the excess of the former over the latter increases, with increasing concentration, from the 0.4 normal, until it reaches 11.5 per cent. in the case of the normal solution. It will also be noted that the ratio of osmotic to gas pressure is the same (1.083) in the 0.1 and 0.8 normal solutions. The anomaly presented by the 0.1 normal solution near its freezing point has been referred to in the previous paper.

The fact that, within the field covered by our experiments, which are summarized in the table, the osmotic pressures are

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[1] The work upon osmotic pressure, which is in progress in this laboratory, is aided by grants from the Carnegie Institution. Up to the present time 24 papers on the subject have been published. They will be found in This Journal, **26**, 80; **28**, 1; **29**, 137; **32**, 93; **34**, 1; **36**, 1 and 39; **37**, 324, 425 and 558; **38**, 175; **39**, 667; **40**, 1, 194, 266 and 325; **41**, 1, 92 and 557; **45**, 91, 237, 283, 517 and 554.

[2] This Journal, **45**, 554.

Table I

	Weight-normal concentration									
	0.1	0.2	0.3	0.4	0.5	0.6	0.7	0.8	0.9	1.0
	Ratio of osmotic to gas pressure									
Temp.										
0°	(1.106)	1.061	1.061	1.060	1.0685	1.0765	1.083	1.093	1.104	1.115
5°	1.082	1.063	1.058	1.059	1.067	1.074	1.084	1.093	1.102	1.115
10°	1.082	1.060	1.059	1.060	1.066	1.073	1.083	1.092	1.102	1.113
15°	1.082	1.061	1.061	1.059	1.068	1.073	1.083	1.093	1.102	1.115
20°	1.084	1.062	1.060	1.060	1.067	1.073	1.084	1.093	1.103	1.115
25°	1.084	1.059	1.060	1.059	1.065	1.071	1.083	1.093	1.102	1.113
Mean	1.083	1.061	1.060	1.060	1.067	1.074	1.083	1.093	1.103	1.114

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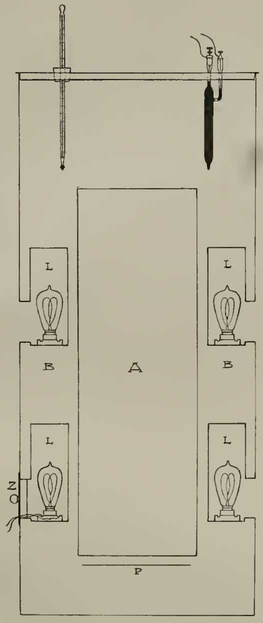

Fig I

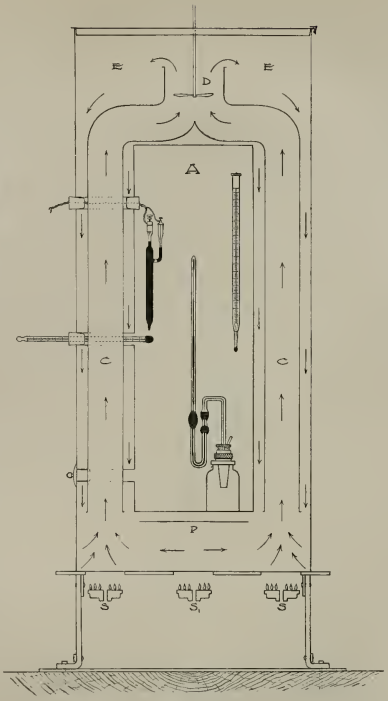

Fig. II

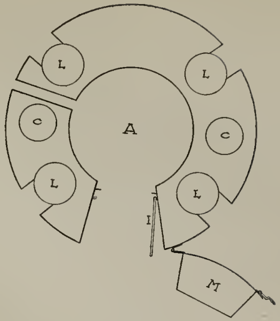

Fig. III

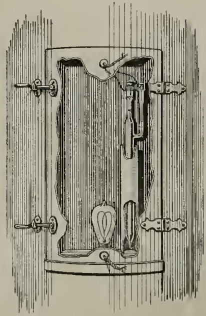

Fig. V

seemingly excessive and not proportional to the supposed concentration of the solutions was not to be accepted as evidence unfavorable to the law of Boyle; for it was conceivable that the apparent anomalies might be due to the unknown molecular relations between the solute and portions of the solvent, which, in effect, cause the solutions to become more concentrated. At all events, it was reasonable to suppose that such relations, if they do exist, would become more simple at higher temperatures. On this account it was deemed important to measure the osmotic pressure of our solutions at temperatures above 25°. This work was already in progress when the last paper was prepared for publication, and we were able to state before closing it "*that the ratios of osmotic to gas pressure, which are so constant for each concentration between 0° and 25°, begin to decline at some temperature between 25° and 30°, and that the rate of decrease is such as to lead one to suspect that the ratios will become unity for all concentrations at temperatures below the boiling point of the solvent.*" In the present paper it will be shown that osmotic and calculated gas pressures become equal in all the concentrations with which we have worked at temperatures not above 80°.

Only one of the baths which were in use when the later work was begun was well adapted to the measurement of osmotic pressure at high temperatures. It was therefore necessary to construct others of a type somewhat different from those described in a recent paper.[1] The new baths are of two sizes, and are made wholly of heavy sheet brass and copper—mainly of the former. *A*, Fig. I, exhibits a section of the inner compartment of one of the smaller baths. It is this compartment which is maintained at any desired constant temperature, and in which the cells are located during a measurement of pressure. It is circular in form in the smaller baths, 300 millimeters in diameter, and one meter in height. Surrounding this is a larger cylinder, *B*,*B*, twice as wide and much higher. In the space between the two brass cylinders the water is heated and made to circulate rapidly over the exterior surface of the inner compartment, *A*. The circulating system and the arrangements for heating the water by gas are shown in Fig. II. *C*,*C* are the pumping tubes, 100 millimeters in diameter, which unite at the top in the short but wider tube *D*. At the bottom, they open directly over the gas stoves *S*,*S*. There is a third gas stove, S_1, which is not ordinarily in use. The water, heated by the stoves *S*,*S*, is pumped up through the tube *C*,*C*, at the rate of about 500 liters per minute. At the top of *D* it is delivered into the space *E*,*E*, and returns to the bottom of the outer cylinder to be reheated and again pumped up through the tubes *C*,*C*. In its downward course, the water passes over the outer surface of *A*, also over the lamp compartments, *L*,*L*,*L*,*L*. In the smaller baths, there are six of these lamp compartments, and in the larger ones, 8. They are distributed in pairs, one in each pair being located directly over the other. The circular openings to the lamp compartments are closed on the outside by means of caps, one of which, *Z*, is shown in Fig. I. Below the inner bath space *A*, Figs. I and II, is the disk *P*, which has nearly the same diameter as the former. It is so placed in order to prevent water which has been heated by the stove S_1 from rising directly against the bottom of *A*. In Fig. II there are also to be seen three tubes, indicated by dotted lines, which serve as passage ways between the exterior and interior for the introduction of thermometer, wires, etc.

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[1] THIS JOURNAL, **45**, 383.

Fig. III is a horizontal section of one of the smaller baths, in which the positions of the pumping tubes are indicated by *C*,*C*, and those of the lamp compartments by *L*,*L*,*L* and *L*. The entrance to the inner bath (150 millimeters in width) is closed by the plate-glass door *I*, and by the hollow metal door *M*. There are two such metal doors, as will be seen in Figs. IV and VI. The lower one, which is opened only when it is necessary to introduce or remove the cells, is packed with hair. The upper door, on the other hand, must be opened whenever an observation is to be made. On this account it is provided with an independent temperature-regulating device, portions of which can be seen in Fig. V. The door is thus prevented from cooling down when open. The space between the inner glass door and the outer metal door is about

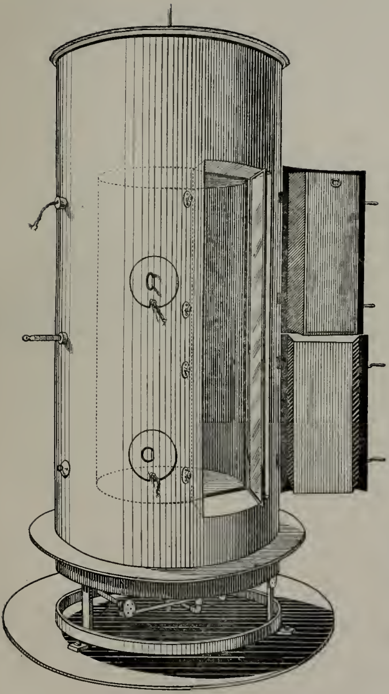

Fig. IV

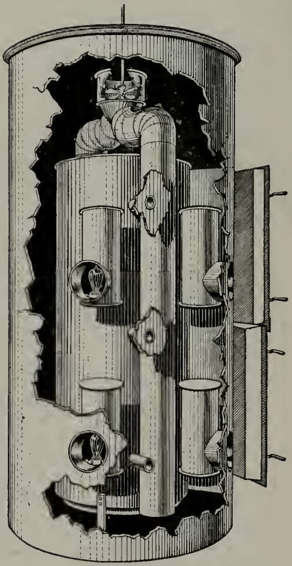

Fig. VI

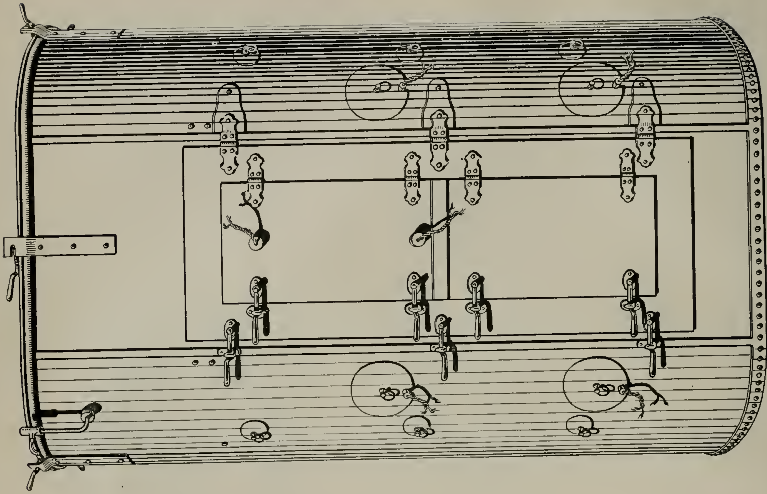

Fig. VIII

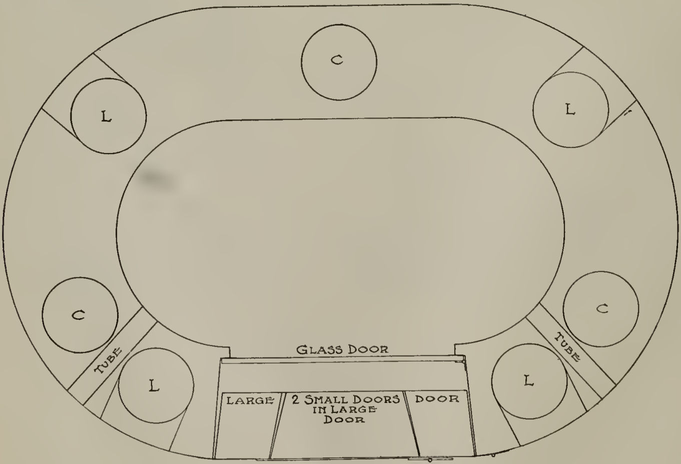

Fig. VII

40 millimeters in width. It is occupied by a brass frame, as large as the glass door, which is filled with minute doors, any one of which can be opened independently of the others. Between this frame, which is placed next to the glass door, and the outer metal doors, is a hair-filled pad, which is so divided that any small portion of the frame may be exposed to view. With these arrangements, it is practicable to read objects in the bath with very slight exposure of the interior. Fig. VI represents the bath with a portion of the exterior removed in order to show the interior relations of the various parts.

Fig. VII is a horizontal section of one of the larger baths which, like those just described, are used for the measurement of osmotic pressure, and also for all the purposes for which the so-called "manometer house"[1] was formerly employed. It is elliptical in form, the longer axis of the interior compartment being twice the diameter of the corresponding part, *A*, in the smaller baths. It has three pumping tubes, *C*,*C* and *C*, instead of two; and 8 lamp compartments, *L*,*L*,*L* and *L*, instead of six. The inner space is ample enough to accommodate the "steel block," the "tappers," and all other appliances which are used in the determination of the capillary depression and the nitrogen volumes of the manometers, and in the comparison of these instruments, one with another. The two smaller metallic doors of the larger bath are like the doors of the smaller bath, except that they are inserted in a larger door which serves them as a frame. The relations of the three doors will be seen in Figs. VII and VIII. The largest door and the lower smaller one are packed with hair, and are opened only when it is necessary to introduce or remove apparatus, or to make some adjustment of the instruments within. The upper smaller door of the larger baths is provided with a device, Fig. V, for the independent regulation of its temperature. It is the only one opened when an observation is to be made. As regards the disposition of the space between the glass and the metal doors, there is no difference between the larger baths and the smaller ones.

Whatever the type of the bath may be which is employed in this investigation, the greatest practicable proportion of the heating is effected by means of gas, and only so much of it is left to the electrical devices as is necessary for effective regulation. Hence, in maintaining the baths just described at temperatures as high as 80°, no lamps of over 16 candle-power are employed. At lower temperatures, lamps of 8 or 10 candle-power suffice. If temperatures but little above that of the room are to be maintained, the electrical appliances only are employed to heat and regulate the baths. For low temperatures, a coil of block-tin pipe is placed in the space *E*,*E*, Fig. II; and through it there is made to circulate, under constant pressure, a current of hydrant water, which has been previously cooled, if necessary.

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[1] This Journal, **45**, 337.

In Fig. II, the thermostat is shown within the compartment *A*, while in Fig. I it is represented as being immersed in the water of the bath. The latter has been found to be the better of the two possible positions for this instrument. The temperature of the water about the thermostat may not be precisely that of the interior compartment, and at other points it may vary slightly; but when the instrument has once been set for a given interior temperature, it is quite capable of maintaining it for any length of time to within 0°.01, which is a rather better regulation than we were able to secure in the older types of baths.

The measurement of osmotic pressure at high temperatures is attended with some difficulties which are not due exclusively to the discomfort of manipulation. Owing to the much lower temperature of the air and of surrounding objects, it is difficult to fill, close and transport the cell to the bath without any appreciable fall in the temperature of the solution. In the same way, the mercury in the manometer cools down during the operations connected with the "setting up" of the cell. When, later, the temperature of the two liquids—the solution and the mercury—has again risen to that of the bath, the compression of the nitrogen, due to their expansion, may exceed the osmotic pressure. If it does, some *concentration* of the solution must ensue. When the over-compression of the nitrogen is minute in comparison with the volume of the solution, the resulting concentration cannot be detected by the polariscope and is, of course, negligible. But the proportion of the experiments in which concentration *can* be detected by the polariscope increases as the work is carried out at the higher temperatures. At moderate temperatures it is rarely detectable.

It is customary, in preparing a cell for the bath, to bring upon the enclosed solution an initial pressure which, together with any additional pressure due to an expected expansion of the liquids, is intended to nearly equal the osmotic pressure. At high temperatures, the allowance made for such expansion is usually insufficient; hence a majority of the cells, after coming to the temperature in the bath, begin their records with pressures which exceed the osmotic pressures of the solutions. As we have shown elsewhere, experiments in which concentration has occurred need not be rejected, provided the exact amount of the concentration can be determined, as it can be, in the case of cane sugar, by means of the polariscope. Nevertheless, we have excluded from the records which follow every experiment, except one, in which concentration could be discovered. In other words, all the solutions of which the records are presented exhibited the same rotations, when removed from the cells, as did other portions of the corresponding original solutions which were reserved for comparison. The exception referred to (Table VIII) is introduced merely to illustrate what may occur when a cell begins its record with a too large over-pressure. The proportion of the whole number of experiments which was excluded in accordance with our rule was less than 10 per cent.

At temperatures above 40°, all glass apparatus which was used in the baths became quite brittle. It was necessary, on this account, to replace the bottles in which the cells are immersed in water during an experiment, and the glasses used in depositing the membranes, with vessels made of copper. The most serious result of the effect of temperature upon the character of the glass was experienced in connection with the manometers. The calibrated portion of these instruments, together with the various bulbs, is detached from the end carrying the "cone" whenever any manipulation of the latter is necessary which might endanger the really valuable part of the manometer. Afterwards, the detached portion is again fused onto the tube which passes through the cone. Owing to the necessity of renewing the rubber on the cone after each experiment, and of frequently "resetting" the tube in the cone with fusible metal, the operation is a constantly recurring one. At moderate temperatures, it gives no trouble, but above 40° the glass of the manometer becomes so brittle that it is necessary carefully to "anneal" the instrument before the operation can be carried out successfully.

In the work between 0° and 25°, the osmotic pressure of the usual 10 concentrations of solution was determined at intervals of 5 degrees, namely, at 0°, 5°, 10°, 15°, 20° and 25°. In the present investigation, the intervals of temperature, after passing 30°, have been doubled. The work at 30°, 40°, 50° and 60° is finished, while that at 70° and 80° is still incomplete. The first question to be answered was: "*At what temperature does the osmotic pressure of each of the 10 concentrations become equal to the calculated gas pressure of the solute?*" That question has been answered definitely, and to this extent the investigation is complete and ready for publicity. There remains to be answered a second question, namely, *whether, when at some temperature the osmotic and calculated gas pressures have become equal, the same relation is maintained at still higher temperatures.* The data which follow furnish only a partial answer to the second question.

The membranes in some of the cells employed in the present investigation had been in use for more than two years, and had acquired in a marked degree the characteristics of *maturity.* These are (1) *reliability,* in the sense that they never give way and become leaky under pressure; and (2) *slowness,* in the sense that the water which must be added to or rather abstracted from the solutions in order to establish equilibrium, requires much time for its passage through the membrane material. They respond very slowly to fluctuations in the volume of the solutions and to changes in atmospheric pressure; in short, they are especially subject to "*ther-*

mometer" and "*barometer effects*." The remedy is to allow cells containing "*mature*" membranes to make long records in the bath, and to correct the mean total pressure of the several days for the mean barometer of the same period. The records will show that the remedy has been applied. The cells have been allowed to remain in the baths much longer than is necessary when the membranes are comparatively fresh; and the *mean* barometer correction has been applied in all cases.

Wherever the cell has required five days or more in order to establish the final equilibrium—within the range of *thermometer* and *barometer effects*—a "preliminary record" for the period has been given. The preliminary record is, however, not always strictly reliable; for during the preliminary period we sometimes test the cell by attempting to turn up the tightening collar, and this treatment is usually followed by a slight increase in the pressure. Such manipulation is never resorted to after the cell has begun its "final" record.

Table II

0.1 Wt. normal solution. Expt. 1 at 30°. Cell Ni_2. Resistance of membrane (nickel ferrocyanide), 500,000 ohms. Manometer 1. Calc. gas pressure, 2.472 atms. Time of setting up cell, April 6, 1911. Barometer during final record: max., 1.010; min., 0.990. Total pressures (daily):

Preliminary Record

	Atms.		Atms.		Atms.
April 8,	3.713	April 13,	3.637	April 17,	3.528
9,	3.711	14,	3.580	18,	3.526
10,	3.702	15,	3.557	19,	3.492
11,	3.687	16,	3.525	20,	3.493
12,	3.660				

(13 days)

Final Record

	Atms.		Atms.		Atms.
April 21,	3.482	April 25,	3.477	April 28,	3.484
22,	3.465	26,	3.481	29,	3.467
23,	3.492	27,	3.482	30,	3.463
24,	3.488				

(10 days)

Mean total pressure, April 21–30 = 3.4781 atms.
Mean barom. pressure, April 21–30 = 1.0025 atms.
Mean osmot. pressure, April 21–30 = 2.4756 atms.

Table III

0.1 Wt. normal solution. Expt. 2 at 30°. Cell K_3. Resistance, 250,000 ohms. Manometer 15. Calc. gas pressure, 2.472 atms. Time of setting up cell, November 13, 1911. Barometer during final record: max., 1.009; min., 0.982. Total daily pressures:

Final Record

	Atms.		Atms.		Atms.
Nov. 14,	3.482	Nov. 18,	3.462	Nov. 22,	3.474
15,	3.468	17,	3.466	23,	3.475
16,	3.463	20,	3.462	24,	3.475
17,	3.465	21,	3.466	(11 days)	

Mean total pressure, Nov. 14–24 = 3.4681 atms.
Mean barom. pressure, Nov. 14–24 = 0.996 atms.
Mean osmot. pressure, Nov. 14–24 = 2.4721 atms.

Table IV

0.1 Wt. normal solution. Expt. 3 at 30°. Cell F_5. Resistance, 209,000 ohms. Manometer 24. Calc. gas pressure, 2.472 atms. Time of setting up cell, November 24, 1911. Barometer during final record: max., 1.013; min., 0.984. Total daily pressures:

Final Record

	Atms.		Atms.		Atms.
Nov. 27,	3.468	Dec. 1,	3.464	Dec. 4,	3.476
28,	3.461	2,	3.469	5,	3.480
29,	3.458	3,	3.472	6,	3.483
30,	3.461			(10 days)	

Mean total pressure, Nov. 27–Dec. 6 = 3.4692 atms.
Mean barom. pressure, Nov. 27–Dec. 6 = 1.001 atms.
Mean osmot. pressure, Nov. 27–Dec. 6 = 2.4682 atms.

Table V

0.1 Wt. normal solution. Expt. 4 at 30°. Cell L_5. Resistance, 159,000 ohms. Manometer 15. Calc. gas pressure, 2.472 atms. Time of setting up cell, November 24, 1911. Barometer during final record: max., 1.013; min., 0.996. Total daily pressures:

Final Record

	Atms.		Atms.		Atms.
Nov. 25,	3.461	Nov. 29,	3.484	Dec. 3,	3.481
26,	3.465	30,	3.489	4,	3.484
27,	3.479	Dec. 1,	3.492	5,	3.485
28,	3.484	2,	3.484	6,	3.491
				(12 days)	

Mean total pressure, Nov. 25–Dec. 6 = 3.4816 atms.
Mean barom. pressure, Nov. 25–Dec. 6 = 1.002 atms.
Mean osmot. pressure, Nov. 25–Dec. 6 = 2.4796 atms.
Mean osmotic pressure for Expts. 1, 2, 3 and 4 = 2.474 atms.
Ratio of osmotic to calc. gas pressure = 1.000

Table VI

0.1 Wt. normal solution. Expt. 1 at 40°. Cell E_5. Resistance, 600,000 ohms. Manometer 9. Calc. gas pressure, 2.553 atms. Time of setting up cell, April 3, 1911. Barometer during final record: max., 1.017; min., 0.994. Total daily pressures:

Preliminary Record

	Atms.		Atms.		Atms.
April 4,	3.709	April 6,	3.680	April 8,	(not recorded)
5,	3.701	7,	(not recorded)		(5 days)

Final Record

	Atms.		Atms.		Atms.
April 9,	3.563	April 13,	3.567	April 16,	3.553
10,	3.568	14,	3.564	17,	3.552
11,	3.567	15,	3.559	18,	3.546
12,	3.567				(10 days)

Mean total pressure, Apr. 9–18 = 3.5606 atms.
Mean barom. pressure, Apr. 9–18 = 1.006 atms.
Mean osmot. pressure, Apr. 9–18 = 2.5546 atms.

Table VII

0.1 Wt. normal solution. Expt. 2 at 40°. Sell F_5. Resistance, 95,000 ohms. Manometer 24. Calc. gas pressure, 2.553 atms. Time of setting up cell, April 3, 1911. Barometer during final record: max., 1.017; min., 0.994. Total daily pressures:

Preliminary Record

	Atms.		Atms.		Atms.
Apr. 4,	4.473	Apr. 6,	3.849	Apr. 3,	3.615
5,	4.048	7,	3.687		(5 days)

Final Record

	Atms.		Atms.		Atms.
Apr. 9,	3.563	Apr. 13,	3.588	Apr. 17,	3.552
10,	3.578	14,	3.575	18,	3.546
11,	3.577	15,	3.571		(10 days)
12,	3.581	16,	3.565		

Mean total pressure, Apr. 9–18 = 3.5696 atms.
Mean barom. pressure, Apr. 9–18 = 1.008 atms.
Mean osmot. pressure, Apr. 9–18 = 2.5616 atms.

Table VIII.—(Example of Concentration in the Cell)

0.1 Wt. normal solution. Expt. 3 at 40°. Cell D_5. Resistance of membrane, 120,000 ohms. Manometer 22. Calc. gas pressure, 2.553 atms. Time of setting up cell, April 3, 1911. Barometer during final record: max., 1.017; min., 0.995. Total daily pressures:

Preliminary Record

	Atms.		Atms.		Atms.
Apr. 4,	4.065	Apr. 6,	3.770	Apr. 8,	3.670
5,	3.815	7,	3.698		(5 days)

Final Record

	Atms.		Atms.		Atms.
Apr. 9,	3.663	Apr. 12,	3.661	Apr. 15,	3.646
10,	3.657	13,	3.656	16,	3.644
11,	3.657	14,	3.546	17,	3.637

Mean total pressure, Apr. 9–17 = 3.652 atms.
Mean barom. pressure, Apr. 9–17 = 1.008 atms.
Mean osmot. pressure, Apr. 9–17 = 2.644 atms.

Gain in rotation = 0°.45 = 0.081 atm. Corrected osmotic pressure = 2.563 atms. Mean osmotic pressure for Experiments 1, 2 and 3 = 2.5597 atms. Ratio of osmotic to gas pressure = 1.003.

Table IX

0.1 Wt. normal solution. Expt. 1 at 50°. Cell U_5. Resistance, 55,000 ohms. Manometer 1. Calc. gas pressure, 2.635 atms. Time of setting up cell, Dec. 7, 1911. Barometer during final record: max., 1.014; min., 0.981. Total daily pressures:

Preliminary Record

	Atms.		Atms.		Atms.
Dec. 8,	3.927	Dec. 11,	3.775	Dec. 14,	3.729
9,	3.831	12,	3.774	15,	3.718
10,	3.791	13,	3.728	16,	3.686

Final Record

	Atms.		Atms.		Atms.
Dec. 17,	3.650	Dec. 21,	3.649	Dec. 25,	3.650
18,	3.646	22,	3.644	26,	3.644
19,	3.643	23,	3.646	27,	3.643
20,	3.648	24,	3.650	28,	3.644

Mean total pressure, Dec. 17–28 = 3.646 atms.
Mean barom. pressure, Dec. 17–28 = 1.003 atms.
Mean osmot. pressure, Dec. 17–28 = 2.643 atms.

Table X

0.1 Wt. normal solution. Expt. 2 at 50°. Cell E_5. Resistance, 100,000 ohms. Manometer 15. Calc. gas pressure, 2.635 atms. Time of setting up cell, Dec. 8, 1911. Barometer during final record: max., 1.014; min., 0.989. Total daily pressures:

Preliminary Record

	Atms.		Atms.		Atms.
Dec. 9,	4.766	Dec. 12,	3.766	Dec. 15,	3.671
10,	4.523	13,	3.744	16,	3.666
11,	4.380	14,	3.713		(8 days)

Final Record

	Atms.		Atms.		Atms.
Dec. 17,	3.644	Dec. 21,	3.642	Dec. 24,	3.635
18,	3.637	22,	3.637	25,	3.635
19,	3.642	23,	3.635	26,	3.635
20,	3.646				(10 days)

Mean total pressure, Dec. 17–26 = 3.6388 atms.
Mean barom. pressure, Dec. 17–26 = 1.005 atms.
Mean osmot. pressure, Dec. 17–27 = 2.6338 atms.

Table XI

0.1 Wt. normal solution. Expt. 3 at 50°. Cell V_5. Resistance, 110,000 ohms. Manometer 9. Calc. gas pressure, 2.635 atms. Time of setting up cell, Dec. 12, 1911. Barometer during final record: max., 1.014; min., 0.981. Total daily pressures:

Preliminary Record

	Atms.		Atms.		Atms.
Dec. 13,	4.203	Dec. 15,	3.419	Dec. 17,	3.654
14,	3.417	16,	3.712[1]		

Final Record

	Atms.		Atms.		Atms.
Dec. 18,	3.632	Dec. 22,	3.629	Dec. 26,	3.630
19,	3.627	23,	3.629	27,	3.624
20,	(not rec'd)	24,	3.629	28,	3.629
21,	(not rec'd)	25,	3.630		(11 days)

Mean total pressure, Dec. 18–28 = 3.629 atms.
Mean. barom. pressure, Dec. 18–28 = 1.000 atm.
Mean osmot. pressure, Dec. 18–28 = 2.629 atms.
Mean osmotic pressure of Expts. 1, 2 and 3 = 2.6353 atms.
Ratio of osmotic to gas pressure = 1.000

[1] Manometer tightened.

Table XII

0.1 Wt. normal solution. Expt. 1 at 60°. Cell W_5. Resistance, 37,000 ohms. Manometer 15. Calc. gas pressure, 2.717 atms. Time of setting up cell, Feb. 15, 1912. Barometer during final record: max., 1.018; min., 0.983. Total daily pressures:

Preliminary Record

	Atms.		Atms.		Atms.
Feb. 16,	4.897	Feb. 19,	4.189	Feb. 22,	3.866
17,	4.622	20,	4.325	23,	3.788
18,	4.408	21,	3.927	24,	3.770

Final Record

	Atms.		Atms.		Atms.
Feb. 25,	3.724	Feb. 29,	3.720	Mar. 3,	3.732
26,	3.721	Mar. 1,	3.729	4,	3.730
27,	3.720	2,	3.731	5,	3.731
28,	3.714				

Mean total pressure, Feb. 25–Mar. 5 = 3.7252 atms.
Mean barom. pressure, Feb. 25–Mar. 5 = 1.005 atms.
Mean osmot. pressure, Feb. 25–Mar. 5 = 2.7202 atms.

Table XIII

0.1 Wt. normal solution. Expt. 2 at 60°. Cell B_5. Resistance, 37,000 ohms. Manometer 11. Calc. gas pressure, 2.717 atms. Time of setting up cell, Feb. 15, 1912. Barometer during final record: max., 1.018; min., 0.983. Total daily pressures:

Preliminary Record

	Atms.		Atms.		Atms.
Feb. 16,	4.520	Feb. 19,	4.122	Feb. 22,	3.898
17,	4.346	20,	4.002	23,	3.780
18,	4.310	21,	3.960	24,	3.787

Final Record

	Atms.		Atms.		Atms.
Feb. 25,	3.718	Feb. 29,	3.713	Mar. 4,	3.726
26,	3.719	Mar. 1,	3.718	5,	3.726
27,	3.716	2,	3.722		(10 days)
28,	3.708	3,	3.726		

Mean total pressure, Feb. 25–Mar. 5 = 3.7192 atms.
Mean barom. pressure, Feb. 25–Mar. 5 = 1.005 atms.
Mean osmot. pressure, Feb. 25–Mar. 5 = 2.7142 atms.
Mean osmotic pressure of Expts. 1 and 2 = 2.7172 atms.
Ratio of osmotic to gas pressure = 1.000

Table XIV

0.2 Wt. normal solution. Expt. 1 at 30°. Cell C_5. Resistance, 120,000 ohms. Manometer 9. Calc. gas pressure, 4.943 atms. Time of setting up cell, October 30, 1911. Barometer during final record: max., 1.018; min., 0.989. Total daily pressures:

Final Record

	Atms.		Atms.		Atms.
Nov. 2,	6.049	Nov. 6,	6.045	Nov. 9,	6.046
3,	6.031	7,	6.045	10,	6.046
4,	6.039	8,	6.044	11,	6.046
5,	6.046				(10 days)

Mean total pressure, Nov. 2–11 = 6.0437 atms.
Mean barom. pressure, Nov. 2–11 = 1.004 atms.
Mean osmot. pressure, Nov. 2–11 = 5.0397 atms.

Table XV

0.2 Wt. normal solution. Expt. 2 at 30°. Cell L_5. Resistance, 150,000 ohms. Manometer 20. Calc. gas pressure, 4.943 atms. Time of setting up cell, October 30, 1911. Barometer during final record: max., 1.018; min., 0.989. Total daily pressures:

Final Record

	Atms.		Atms.		Atms.
Nov. 3,	6.056	Nov. 7,	6.042	Nov. 11,	6.041
4,	6.052	8,	6.040	12,	6.039
5,	6.050	9,	6.038	13,	6.053
6,	6.046	10,	6.041		(11 days)

Mean total pressure, Nov. 3–13 = 6.0498 atms.
Mean barom. pressure, Nov. 3–13 = 1.002 atms.
Mean osmot. pressure, Nov. 3–13 = 5.0478 atms.
Mean osmotic pressure for Expts. 1 and 2 = 5.0438 atms.
Ratio of osmotic to gas pressure = 1.020

Table XVI

0.2 Wt. normal solution. Expt. 1 at 40°. Cell I_5. Resistance, 120,000 ohms. Manometer 11. Calc. gas pressure, 5.106 atms. Time of setting up cell, March 22, 1911. Barometer during final record: max., 1.016; min., 0.974. Total daily pressures:

Final Record

	Atms.		Atms.		Atms.
Mar. 24,	6.176	Mar. 27,	(not rec'd)	Mar. 30,	6.150
25,	6.159	28,	6.169	31,	6.147
26,	6.179	29,	(not rec'd)	Apr. 1,	6.166

Mean total pressure, Mar. 24–Apr. 1 = 6.164 atms.
Mean barom. pressure, Mar. 24–Apr. 1 = 0.996 atms.
Mean osmot. pressure, Mar. 24–Apr. 1 = 5.168 atms.

Table XVII

0.2 Wt. normal solution. Expt. 2 at 40°. Cell P$_3$. Resistance, 150,000 ohms. Manometer 5. Calc. gas pressure, 5.106 atms. Time of setting up cell, March 22, 1911. Barometer during final record: max., 1.016; min., 0.997. Total daily pressures:

Preliminary Record

	Atms.		Atms.		Atms.
Mar. 24,	6.715	Mar. 29,	6.307	Apr. 3,	(not rec'd)
25,	6.600	30,	6.236	4,	6.193
26,	6.505	31,	6.228	5,	6.204
27,	6.412	Apr. 1,	6.268	6,	6.192
28,	6.319	2,	6.282	7,	6.178

Final Record

	Atms.		Atms.		Atms.
Apr. 8,	6.162	Apr. 10,	6.180	Apr. 12,	6.166
9,	6.162	11,	6.176	13,	6.165

Mean total pressure, April 8–13 = 6.1685 atms.
Mean barom. pressure, April 8–13 = 1.0105 atms.
Mean osmot. pressure, April 8–13 = 5.158 atms.
Mean osmotic pressure of Expts. 1 and 2 = 5.163 atms.
Ratio of osmotic to gas pressure = 1.011

Table XVIII

0.2 Wt. normal solution. Expt. 1 at 50°. Cell L$_5$. Resistance, 75,000 ohms. Manometer 29. Calc. gas pressure, 5.27 atms. Time of setting up cell, November 28, 1911. Barometer during final record: max., 1.011; min., 0.997. Total daily pressures:

Preliminary Record

	Atms.		Atms.		Atms.
Nov. 29,	7.552	Dec. 1,	6.518	Dec. 3,	6.186
30,	(not rec'd)	2,	6.165		

Final Record

	Atms.		Atms.		Atms.
Dec. 4,	6.281	Dec. 8,	6.284	Dec. 11,	6.285
5,	6.263	9,	6.285	12,	6.288
6,	6.277	10,	6.283	13,	6.287
7,	6.280				(10 days)

Mean total pressure, Dec. 4–13 = 6.2813 atms.
Mean barom. pressure, Dec. 4–13 = 1.008 atms.
Mean osmot. pressure, Dec. 4–13 = 5.2733 atms.

Table XIX

0.2 Wt. normal solution. Expt. 2 at 50°. Cell S_5. Resistance, 65,000 ohms. Manometer 39. Calc. gas pressure, 5.27 atms. Time of setting up cell, November 28, 1911. Barometer during final record: max., 1.011; min., 0.997. Total daily pressures:

Preliminary Record

	Atms.		Atms.		Atms.
Nov. 29,	6.221	Dec. 1,	6.181	Dec. 3,	6.058
30,	(not rec'd)	2,	6.231	4,	6.244

Final Record

	Atms.		Atms.		Atms.
Dec. 5,	6.266	Dec. 9,	6.300	Dec. 12,	6.301
6,	6.290	10,	6.300	13,	6.299
7,	6.300	11,	6.300	14,	6.295
8,	6.299				(10 days)

Mean total pressure, Dec. 5–14 = 6.295 atms.
Mean barom. pressure, Dec. 5–14 = 1.009 atms.
Mean osmot. pressure, Dec. 5–14 = 5.285 atms.

Table XX

0.2 Wt. normal solution. Expt. 3 at 50°. Cell R_5. Resistance, 80,000 ohms. Manometer 27. Calc. gas pressure, 5.27 atms. Time of setting up cell, November 28, 1911. Barometer during final record: max., 1.001; min., 0.997. Total daily pressures:

Final Record

	Atms.		Atms.		Atms.
Dec. 3,	6.274	Dec. 7,	6.277	Dec. 11,	6.283
4,	6.316	8,	6.279	12,	6.279
5,	6.284	9,	6.282	13,	6.282
6,	6.284	10,	6.279		(11 days)

Mean total pressure, Dec. 3–13 = 6.284 atms.
Mean barom. pressure, Dec. 3–13 = 1.007 atms.
Mean osmot. pressure, Dec. 3–13 = 5.277 atms.
Mean osmotic pressure of Expts. 1, 2 and 3 = 5.2784 atms.
Ratio of osmotic to gas pressure = 1.0016

Table XXI

0.2 Wt. normal solution. Expt. 1 at 60°. Cell E_5. Resistance, 50,000 ohms. Manometer 1. Calc. gas pressure, 5.433 atms. Time of setting up cell, February 7, 1911. Barometer during final record: max., 1.013; min., 0.982. Total daily pressures:

Preliminary Record

	Atms.		Atms.		Atms.
Feb. 8,	6.563	Feb. 10,	6.527	Feb. 12,	6.496
9,	6.549	11,	6.510		

Final Record

	Atms.		Atms.		Atms.
Feb. 13,	6.457	Feb. 17,	6.452	Feb. 21,	6.414
14,	6.449	18,	6.445	22,	6.417
15,	6.441	19,	6.444	23,	6.436
16,	6.456	20,	6.449		(11 days)

Mean total pressure, Feb. 13–23 = 6.446 atms.
Mean barom. pressure, Feb. 13–23 = 0.996 atms.
Mean osmot. pressure, Feb. 13–23 = 5.450 atms.

Table XXII

0.2 Wt. normal solution. Expt. 2 at 60°. Cell K_5. Resistance, 61,000 ohms. Manometer 1. Calc. gas pressure, 5.433 atms. Time of setting up cell, February 26, 1911. Barometer during final record: max., 1.013; min., 0.987. Total daily pressures:

Preliminary Record

	Atms.		Atms.		Atms.
Feb. 27,	9.239	Mar. 1,	7.784	Mar. 4,	6.652
28,	8.395	2,	7.222	5,	6.481
29,	8.117	3,	6.930		

Final Record

	Atms.		Atms.		Atms.
Mar. 6,	6.442	Mar. 9,	4.429	Mar. 12,	432.0
7,	6.420	10,	4.430	13,	411.0
9,	6.423	11,	4.427	14,	416.0

Mean total pressure, Mar. 6–14 = 6.4256 atms.
Mean barom. pressure, Mar. 6–14 = 1.001 atms.
Mean osmot. pressure, Mar. 6–14 = 5.4246 atms.
Mean osmotic pressure of Expts. 1 and 2 = 5.4373 atms.
Ratio of osmotic to gas pressure = 1.0008

Table XXIII

0.3 Wt. normal solution. Expt. 1 at 30°. Cell B_5. Resistance, 110,000 ohms. Manometer 11. Calc. gas pressure, 7.415 atms. Time of setting up cell, October 25, 1911. Barometer during final record: max., 1.018; min., 0.989. Total daily pressures:

Preliminary Record

	Atms.		Atms.		Atms.
Oct. 27,	10.185	Oct. 29,	8.845	Oct. 31,	8.703
28,	8.945	30,	8.765	Nov. 1,	8.662

Final Record

	Atms.		Atms.		Atms.
Nov. 2,	8.660	Nov. 6,	8.646	Nov. 9,	8.641
3,	8.654	7,	8.638	10,	8.644
4,	8.640	8,	8.637	11,	8.643
5,	8.646				

Mean total pressure, Nov. 2–11 = 8.6449 atms.
Mean barom. pressure, Nov. 2–11 = 1.004 atms.
Mean osmot. pressure, Nov. 2–11 = 7.6409 atms.

Table XXIV

0.3 Wt. normal solution. Expt. 2 at 30°. Cell H_5. Resistance, 110,000 ohms. Manometer 24. Calc. gas pressure, 7.415 atms. Time of setting up cell, October 25, 1911. Barometer during final record: max., 1.018; min., 0.989. Total daily pressures:

Preliminary Record

	Atms.		Atms.		Atms.
Oct. 27,	8.710	Oct. 30,	8.561	Nov. 1,	8.900
28,	8.594	31,	8.878	2,	8.746
29,	8.573				(7 days)

Final Record

	Atms.		Atms.		Atms.
Nov. 3,	8.685	Nov. 6,	8.668	Nov. 9,	8.652
4.	8.675	7,	8.648	10,	8.652
5,	8.675	8,	8.650	11,	8.651

Mean total pressure, Nov. 3–11 = 8.6556 atms.
Mean barom. pressure, Nov. 3–11 = 1.003 atms.
Mean osmot. pressure, Nov. 3–11 = 7.6526 atms.
Mean of osmotic pressures of Expts. 1 and 2 = 7.6468 atms.
Ratio of osmotic to gas pressure = 1.031

Table XXV

0.3 Wt. normal solution. Expt. 1 at 40°. Cell D_3. Resistance, 80,000 ohms. Manometer 39. Calc. gas pressure, 7.66 atms. Time of setting up cell, April 21, 1911. Barometer during final record: max., 1.009; min., 0.987. Total daily pressures:

Preliminary Record

	Atms.		Atms.		Atms.
Apr. 22,	7.442	Apr. 25,	8.714	Apr. 27,	8.785
23,	8.532	26,	8.747	28,	8.785
24,	8.571				

Final Record

	Atms.		Atms.		Atms.
Apr. 29,	8.805	May 2,	8.795	May 4,	8.814
30,	8.820	3,	8.807	5,	8.817
May 1,	8.834				

Mean total pressure, Apr. 29–May 5 = 8.813 atms.
Mean barom. pressure, Apr. 29–May 5 = 0.997 atm.
Mean osmot. pressure, Apr. 29–May 5 = 7.817 atms.

Table XXVI

0.3 Wt. normal solution. Expt. 2 at 40°. Cell D_5. Resistance, 110,000 ohms. Manometer 22. Calc. gas pressure, 7.66 atms. Time of setting up cell, April 26, 1911. Barometer: max., 1.010; min., 0.985. Total daily pressures:

Final Record

	Atms.		Atms.		Atms.
Apr. 28,	8.849	May 2,	8.854	May 6,	8.865
29,	8.838	3,	8.856	7,	8.874
30,	8.821	4,	8.865	8,	8.859
May 1,	8.849	5,	8.867		

Mean total pressure, Apr. 28–May 8 = 8.854 atms.
Mean barom. pressure, Apr. 28–May 8 = 1.001 atms.
Mean osmot. pressure, Apr. 28–May 8 = 7.853 atms.

Table XXVII

0.3 Wt. normal solutions. Expt. 3 at 40°. Cell E_5. Resistance, 80,000 ohms. Manometer 6. Calc. gas pressure, 7.66 atms. Time of setting up cell, April 26, 1911. Barometer during final record: max., 1.010; min., 0.993. Total daily pressures:

Preliminary Record

	Atms.		Atms.		Atms.
Apr. 27,	7.736	Apr. 29,	8.717	May 1,	8.799
28,	8.457	30,	8.717		

Final Record

	Atms.		Atms.		Atms.
May 2,	8.854	May 5,	8.839	May 7,	8.820
3,	8.828	6,	8.843	8,	8.813
4,	8.844				

Mean total pressure, May 2–8 = 8.834 atms.
Mean barom. pressure, May 2–8 = 1.003 atms.
Mean osmot. pressure, May 2–8 = 7.831 atms.

Table XXVIII

0.3 Wt. normal solution. Expt. 4 at 40°. Cell F_5. Resistance, 110,000 ohms. Manometer 24. Calc. gas pressure, 7.66 atms. Time of setting up cell, April 26, 1911. Barometer: max., 1.010; min., 0.983. Total daily pressures:

Final Record

	Atms.		Atms.		Atms.
Apr. 29,	8.824	May 3,	8.827	May 6,	8.853
30,	(not rec'd)	4,	8.840	7,	8.848
May 1,	(not rec'd)	5,	8.842	8,	8.846
2,	8.808				

Mean total pressure, Apr. 29–May 8 = 8.836 atms.
Mean barom. pressure, Apr. 29–May 8 = 1.001 atms.
Mean osmot. pressure, Apr. 29–May 8 = 7.835 atms.
Mean osmotic pressure of Expts. 1, 2, 3 and 4 = 7.844 atms.
Ratio of osmotic to gas pressure = 1.024

Table XXIX

0.3 Wt. normal solution. Expt. 1 at 50°. Cell B_5. Resistance 75,000 ohms. Manometer 38. Calc. gas pressure, 7.905 atms. Time of setting up cell, December 6, 1911. Barometer during final record: max., 1.013; min., 0.981. Total daily pressures:

Preliminary Record

	Atms.		Atms.		Atms.
Dec. 7,	10.790	Dec. 12,	9.494	Dec. 16,	9.091
8,	10.498	13,	9.336	17,	9.093
9,	10.158	14,	9.249	18,	8.914
10,	9.805	15,	9.091	19,	8.892
11,	9.647				(13 days)

Final Record

	Atms.		Atms.		Atms.
Dec. 20,	8.945	Dec. 23,	8.968	Dec. 26,	8.968
21,	8.950	24,	8.968	27,	8.961
22,	8.962	25,	8.967	28,	8.964

Mean total pressure, Dec. 20–28 = 8.961 atms.
Mean barom. pressure, Dec. 20–28 = 1.001 atms.
Mean osmot. pressure, Dec. 20–28 = 7.960 atms.

Table XXX

0.3 Wt. normal solution. Expt. 2 at 50°. Cell T_5. Resistance, 60,000 ohms. Manometer 5. Calc. gas pressure, 7.905 atms. Time of setting up cell, December 6, 1911. Barometer during final record: max., 1.014; min., 0.991. Total daily pressures:

Preliminary Record

	Atms.		Atms.		Atms.
Dec. 7,	11.358	Dec. 10,	9.131	Dec. 12,	9.050
8,	10.076	11,	9.106	13,	8.934
9,	9.444				

Final Record

	Atms.		Atms.		Atms.
Dec. 14,	9.005	Dec. 18,	8.978	Dec. 21,	9.003
15,	8.995	19,	8.994	22,	8.995
16,	8.976	20,	9.012	23,	8.991
17,	8.980				(10 days)

Mean total pressure, Dec. 14–23 = 8.9929 atms.
Mean barom. pressure, Dec. 14–23 = 1.005 atms.
Mean osmot. pressure, Dec. 14–23 = 7.9879 atms.

Table XXXI

0.3 Wt. normal solution. Expt. 3 at 50°. Cell P_5. Resistance, 75,000 ohms. Manometer 2. Calc. gas pressure, 7.905 atms. Time of setting up cell, December 19, 1911. Barometer during final record: max., 1.009; min., 0.981. Total daily pressures:

Final Record

	Atms.		Atms.		Atms.
Dec. 22,	8.970	Dec. 26,	8.978	Dec. 29,	8.942
23,	8.981	27,	9.001	30,	8.981
24,	8.978	28,	8.959	31,	8.925
25	8.992				(10 days)

Mean total pressure, Dec. 22–31 = 8.9707 atms.
Mean barom. pressure, Dec. 22–31 = 0.997 atm.
Mean osmot. pressure, Dec. 22–31 = 7.9737 atms.
Mean osmotic pressure of Expts. 1, 2 and 3 = 7.9739 atms.
Ratio of osmotic to gas pressure = 1.0087

Table XXXII

0.3 Wt. normal solution. Expt. 1 at 60°. Cell K_5. Resistance, 75,000 ohms. Manometer 15. Calc. gas pressure, 8.150 atms. Time of setting up cell, January 25, 1912. Barometer during final record: max., 1.013; min., 0.995. Total daily pressures:

Preliminary Record

	Atms.		Atms.		Atms.
Jan. 26,	17.252	Jan. 30,	10.314	Feb. 3,	9.253
27,	14.022	31,	9.792	4,	9.210
28,	11.705	Feb. 1,	9.475	5,	9.178
29,	10.960	2,	9.332		(11 days)

Final Record

	Atms.		Atms.		Atms.
Feb. 6,	9.147	Feb. 10,	9.142	Feb. 13,	9.157
7,	9.137	11,	9.151	14,	9.160
8,	9.155	12,	9.161	15,	9.156
9,	9.156				(10 days)

Mean total pressure, Feb. 6–15 = 9.1522 atms.
Mean barom. pressure, Feb. 6–15 = 1.000 atm.
Mean osmot. pressure, Feb. 6–15 = 8.1522 atms.

Table XXXIII

0.3 Wt. normal solutions. Expt. 2 at 60°. Cell F_5. Resistance, 75,000 ohms. Manometer 11. Calc. gas pressure, 8.150 atms. Time of setting up cell, January 25, 1912. Barometer during final record: max., 1.013; min., 0.995. Total daily pressures:

Preliminary Record

	Atms.		Atms.		Atms.
Jan. 26,	9.730	Jan. 30,	9.004	Feb. 3,	9.727
27,	9.274	31,	8.800	4,	9.443
28,	8.837	Feb. 1,	(not rec'd)	5,	9.269
29,	9.025	2,	(not rec'd)		(11 days)

Final Record

	Atms.		Atms.		Atms.
Feb. 6,	9.133	Feb. 10,	9.130	Feb. 13,	9.123
7,	9.153	11,	9.117	14,	9.134
8,	9.136	12,	9.114	15,	9.134
9,	9.109				(10 days)

Mean total pressure, Feb. 6–15 = 9.1283 atms.
Mean barom. pressure, Feb. 6–15 = 1.000 atm.
Mean osmot. pressure, Feb. 6–15 = 8.1283 atms.
Mean osmotic pressure for Expts. 1 and 2 = 8.1403 atms.
Ratio of osmotic to gas pressure = 0.999

Table XXXIV

0.4 Wt. normal solution. Expt. 1 at 30°. Cell L_5. Resistance, 110,000 ohms. Manometer 29. Calc. gas pressure, 9.886 atms. Time of setting up cell, October 13, 1911. Barometer during final record: max., 1.014; min., 0.995. Total daily pressures:

Preliminary Record

	Atms.		Atms.		Atms.
Oct. 14,	12.080	Oct. 16,	11.556	Oct. 18,	11.375
15,	11.518	17,	11.452	19,	11.331

Final Record

	Atms.		Atms.		Atms.
Oct. 20,	11.309	Oct. 22,	11.305	Oct. 24,	11.294
21,	11.313	23,	11.305	25,	11.313

Mean total pressure, Oct. 20–25 = 11.307 atms.
Mean barom. pressure, Oct. 20–25 = 1.002 atms.
Mean osmot. pressure, Oct. 20–25 = 10.305 atms.

Table XXXV

0.4 Wt. normal solution. Expt. 2 at 30°. Cell C_5. Resistance, 250,000 ohms. Manometer 24. Calc. gas pressure, 9.886 atms. Time of setting up cell, October 13, 1911. Barometer during final record: max., 1.014; min., 0.989. Total daily pressures:

Final Record

	Atms.		Atms.		Atms.
Oct. 16,	11.297	Oct. 20,	11.286	Oct. 23,	11.284
17,	11.278	21,	11.287	24,	11.287
18,	11.279	22,	11.284	25,	11.292
19,	11.271				(10 days)

Mean total pressure, Oct. 16–25 = 11.285 atms.
Mean barom. pressure, Oct. 16–25 = 1.000 atm.
Mean osmot. pressure, Oct. 16–25 = 10.285 atms.
Mean osmotic pressure of Expts. 1 and 2 = 10.295 atms.
Ratio of osmotic to gas pressure = 1.040.

Table XXXVI

0.4 Wt. normal solution. Expt. 1 at 40°. Cell D_3. Resistance, 126,000 ohms. Manometer 15. Calc. gas pressure, 10.213 atms. Time of setting up cell, March 14, 1911. Barometer during final record: max., 1.014; min., 0.977. Total daily pressures:

Preliminary Record

	Atms.		Atms.		Atms.
Mar. 15,	10.345	Mar. 18,	11.510	Mar. 20,	11.512
16,	11.047	19,	11.512	21,	11.517
17,	11.370				

Final Record

	Atms.		Atms.		Atms.
Mar. 22,	11.605	Mar. 25,	11.586	Mar. 28,	11.581
23,	11.596	26,	11.566	29,	11.614
24,	11.609	27,	11.599	30,	11.575

Mean total pressure, Mar. 22–30 = 11.593 atms.
Mean barom. pressure, Mar. 22–30 = 0.994 atm.
Mean osmot. pressure, Mar. 22–30 = 10.599 atms.

Table XXXVII

0.4 Wt. normal solution. Expt. 2 at 40°. Cell R_3. Resistance, 205,000 ohms. Manometer 9. Calc. gas pressure, 10.213 atms. Time of setting up cell, March 14, 1911. Barometer during final record: max., 1.011; min., 0.990. Total daily pressures:

Final Record

	Atms.		Atms.		Atms.
Mar. 16,	11.617	Mar. 18,	11.592	Mar. 19,	11.606
17,	11.603				

Mean total pressure, Mar. 16–19 = 11.6045 atms.
Mean barom. pressure, Mar. 16–19 = 1.002 atms.
Mean osmot. pressure, Mar. 16–19 = 10.6025 atms.

Table XXXVIII

0.4 Wt. normal solution. Expt. 3 at 40°. Cell N_3. Resistance, 190,000 ohms. Manometer 6. Calc. gas pressure, 10.213 atms. Time of setting up cell, March 14, 1911. Barometer during final record: max., 1.016; min., 0.990. Total daily pressures:

Preliminary Record

	Atms.		Atms.		Atms.
Mar. 15,	14.135	Mar. 18,	12.292	Mar. 20,	11.724
16,	13.359	19,	11.838	21,	(not rec'd)
17,	12.770				

Final Record

	Atms.		Atms.		Atms.
Mar. 22,	11.612	Mar. 24,	11.620	Mar. 26,	11.615
23,	11.583	25,	11.621	27,	11.607

Mean total pressure, Mar. 22–27 = 11.6097 atms.
Mean barom. pressure, Mar. 22–27 = 1.003 atms.
Mean osmot. pressure, Mar. 22–27 = 10.6067 atms.

Table XXXIX

0.4 Wt. normal solution. Expt. 4 at 40°. Cell I_5. Resistance, 120,000 ohms. Manometer 5. Calc. gas pressure, 10.213 atms. Time of setting up cell, March 11, 1911. Barometer during final record: max., 1.012; min., 0.992. Total daily pressures:

Final Record

	Atms.		Atms.		Atms.
Mar. 12,	11.562	Mar. 15,	11.568	Mar. 17,	11.567
13,	11.621	16,	11.596	18,	11.577
14,	11.621				

Mean total pressure, Mar. 12–18 = 11.5874 atms.
Mean barom. pressure, Mar. 12–18 = 1.001 atms.
Mean osmot. pressure, Mar. 12–18 = 10.5864 atms.
Mean osmotic pressure for Expts. 1,2, 3 and 4 = 10.5987 atms.
Ratio of osmotic to gas pressure = 1.0377

Table XL

0.4 Wt. normal solution. Expt. 1 at 50°. Cell S_5. Resistance, 71,000 ohms. Manometer 38. Calc. gas pressure, 10.540 atms. Time of setting up cell, January 4, 1912. Barometer during final record: max., 1.019; min., 0.988. Total daily pressures:

Preliminary Record

	Atms.		Atms.		Atms.
Jan. 5,	13.451	Jan. 7,	12.088	Jan. 9,	11.878
6,	12.838	8,	(not rec'd)	10,	11.833

Final Record

	Atms.		Atms.		Atms.
Jan. 11,	11.750	Jan. 15,	11.742	Jan. 18,	11.731
12,	11.759	16,	11.738	19,	11.725
13,	11.750	17,	11.732	20,	11.726
14,	11.748				(10 days)

Mean total pressure, Jan. 11–20 = 11.740 atms.
Mean barom. pressure, Jan. 11–20 = 1.003 atms.
Mean osmot. pressure, Jan. 11–20 = 10.737 atms.

Table XLI

0.4 Wt. normal solution. Expt. 2 at 50°. Cell H_5. Resistance, 190,000 ohms. Manometer 4. Calc. gas pressure, 10.540 atms. Time of setting up cell, January 4, 1912. Barometer during final record: max., 1.019; min., 0.988. Total daily pressures:

Preliminary Record

	Atms.		Atms.		Atms.
Jan. 5,	12.309	Jan. 7,	11.906	Jan. 9,	10.827
6,	11.955	8,	11.853	10,	(not rec'd)

Final Record

	Atms.		Atms.		Atms.
Jan. 11,	11.695	Jan. 15,	11.724	Jan. 18,	11.711
12,	11.704	16,	11.711	19,	11.702
13,	11.718	17,	11.713	20,	11.724
14,	11.729				(10 days)

Mean total pressure, Jan. 11–20 = 11.713 atms.
Mean barom. pressure, Jan. 11–20 = 1.003 atms.
Mean osmot. pressure, Jan. 11–20 = 10.710 atms.
Mean osmotic pressure for Expts. 1 and 2 = 10.724 atms
Ratio of osmotic to gas pressure = 1.017

Table XLII

0.4 Wt. normal solution. Expt. 1 at 60°. Cell G_5. Resistance, 28,000 ohms. Manometer 39. Calc. gas pressure, 10.867 atms. Time of setting up cell, February 12, 1912. Barometer during final record: max., 1.018; min., 0.983. Total daily pressures:

Preliminary Record

	Atms.		Atms.		Atms.
Feb. 13,	16.075	Feb. 17,	11.955	Feb. 20,	13.281
14,	13.964	18,	11.789	21,	12.043
15,	12.822	19,	14.031[1]	22,	12.040
16,	12.335				

Final Record

	Atms.		Atms.		Atms.
Feb. 23,	11.892	Feb. 27,	11.877	Mar. 2,	11.885
24,	11.858	28,	11.869	3,	11.886
25,	11.868	29,	11.874	4,	11.887
26,	11.853	Mar. 1,	11.886		(11 days)

Mean total pressure, Feb. 23–Mar. 4 = 11.876 atms.
Mean barom. pressure, Feb. 23–Mar. 4 = 1.005 atms.
Mean osmot. pressure, Feb. 23–Mar. 4 = 10.871 atms.

Table XLIII

0.4 Wt. normal solution. Expt. 2 at 60°. Cell F_3. Resistance, 57,500 ohms. Manometer 5. Calc. gas pressure, 10.867 atms. Time of setting up cell, February 26, 1912. Barometer during final record: max., 1.018; min., 0.994. Total daily pressures:

Preliminary Record

	Atms.		Atms.		Atms.
Feb. 27,	11.578	Feb. 29,	12.744[2]	Mar. 2,	11.948
28,	11.394	Mar. 1,	12.176		

Final Record

	Atms.		Atms.		Atms.
Mar. 3,	11.889	Mar. 6,	11.858	Mar. 9,	11.850
4,	11.862	7,	11.848	10,	11.862
5,	11.882	8,	11.827	11,	11.858

Mean total pressure, Mar. 3–11 = 11.860 atms.
Mean barom. pressure, Mar. 3–11 = 1.007 atms.
Mean osmot. pressure, Mar. 3–11 = 10.853 atms.

[1] Manometer cone screwed down.

[2] Cone tightened.

Table XLIV

0.4 Wt. normal solution. Expt. 3 at 60°. Cell C_5. Resistance, 16,000 ohms. Manometer 2. Calc. gas pressure, 10.867 atms. Time of setting up cell, February 26, 1912. Barometer during final record: max., 1.018; min., 0.994. Total daily pressures:

Final Record

	Atms.		Atms.		Atms.
Feb. 29,	11.900	Mar. 4,	11.863	Mar. 7,	11.886
Mar. 1,	11.858	5,	11.877	8,	11.890
2,	11.891	6,	11.890	9,	11.880
3,	11.890				(10 days)

Mean total pressure, Feb. 29–Mar. 9 = 11.883 atms.
Mean barom. pressure, Feb. 29–Mar. 9 = 1.010 atms.
Mean osmot. pressure, Feb. 29–Mar. 9 = 10.873 atms.

Mean osmotic pressure for Expts. 1, 2 and 3 = 10.866 atms.

Ratio of osmotic to gas pressure = 1.000

Table XLV

0.5 Wt. normal solution. Expt. 1 at 30°. Cell I_5. Resistance, 110,000 ohms. Manometer 4. Calc. gas pressure, 12.358 atms. Time of setting up cell, October 10, 1911. Barometer during final record: max., 1.014; min., 0.989. Total daily pressures:

Preliminary Record

	Atms.		Atms.		Atms.
Oct. 11,	16.618	Oct. 13,	14.771	Oct. 15,	14.169
12,	15.442	14,	14.452	16,	14.097

Final Record

	Atms.		Atms.		Atms.
Oct. 17,	13.996	Oct. 20,	13.974	Oct. 23,	13.974
18,	13.976	21,	13.976	24,	13.990
19,	13.966	22,	13.972	25,	14.000

Mean total pressure, Oct. 17–25 = 13.9804 atms.
Mean barom. pressure, Oct. 17–25 = 1.000 atm.
Mean osmot. pressure, Oct. 17–25 = 12.9804 atms.

Table XLVI

0.5 Wt. normal solution. Expt. 2 at 30°. Cell O_5. Resistance, 100,000 ohms. Manometer 15. Calc. gas pressure, 12.358 atms. Time of setting up cell, October 19, 1911. Barometer during final record: max., 1.014; min., 0.995. Total daily pressures:

Final Record

	Atms.		Atms.		Atms.
Oct. 21,	13.962	Oct. 25,	13.986	Oct. 28,	13.986
22,	13.971	26,	13.981	29,	13.981
23,	13.975	27,	13.982	30,	13.981
24,	13.979				(10 days)

Mean total pressure, Oct. 21–30 = 13.9784 atms.
Mean barom. pressure, Oct. 21–30 = 1.003 atms.
Mean osmot. pressure, Oct. 21–30 = 12.9754 atms.
Mean osmotic pressure for Expts. 1 and 2 = 12.9779 atms.
Ratio of osmotic to gas pressure = 1.050

Table XLVII

0.5 Wt. normal solution. Expt. 1 at 40°. Cell A_5. Resistance, 100,000 ohms. Manometer 9. Calc. gas pressure, 12.767 atms. Time of setting up cell, March 29, 1911. Barometer during final record: max., 1.009; min., 0.989. Total daily pressures:

Final Record

	Atms.		Atms.		Atms.
Mar. 31,	14.359	Apr. 2,	14.338	Apr. 3,	14.334
Apr. 1,	14.363				

Mean total pressure, Mar. 31–Apr. 3 = 14.349 atms.
Mean barom. pressure, Mar. 31–Apr. 3 = 1.000 atm.
Mean osmot. pressure, Mar. 31–Apr. 3 = 13.349 atms.

Table XLVIII

0.5 Wt. normal solution. Expt. 2 at 40°. Cell B_5. Resistance, 80,000 ohms. Manometer 24. Calc. gas pressure, 12.767 atms. Time of setting up cell, March 29, 1911. Barometer during final record: max., 1.009; min., 0.989. Total daily pressures:

Final Record

	Atms.		Atms.		Atms.
Mar. 31,	14.346	Apr. 2,	14.381	Apr. 3,	14.378
Apr. 1,	14.338				

Mean total pressure, Mar. 31–Apr. 3 = 14.361 atms.
Mean barom. pressure, Mar. 31–Apr. 3 = 1.000 atms.
Mean osmot. pressure. Mar. 31–Apr. 3 = 13.361 atms.
Mean osmotic pressure for Expts. 1 and 2 = 13.355 atms.
Ratio of osmotic to gas pressure = 1.046

Table XLIX

0.5 Wt. normal solution. Expt. 1 at 50°. Cell I_5. Resistance, 81,000 ohms. Manometer 1. Calc. gas pressure, 13.175 atms. Time of setting up cell, January 4, 1912. Barometer: max., 1.019; min., 0.988. Total daily pressures:

Preliminary Record

	Atms.		Atms.		Atms.
Jan. 5,	18.777	Jan. 7,	14.916	Jan. 9,	(not rec'd)
6,	15.851	8,	14.831		

Final Record

	Atms.		Atms.		Atms.
Jan. 10,	14.534	Jan. 14,	14.501	Jan. 17,	14.493
11,	14.511	15,	14.512	18,	14.496
12,	14.541	16,	14.527	19,	14.512
13,	14.541				(10 days)

Mean total pressure, Jan. 10–19 = 14.5168 atms.
Mean barom. pressure, Jan. 10–19 = 1.002 atms.
Mean osmot. pressure, Jan. 10–19 = 13.5148 atms.

Table L

0.5 Wt. normal solution. Expt. 2 at 50°. Cell F_3. Resistance, 377,000 ohms. Manometer 29. Calc. gas pressure, 13.175 atms. Time of setting up cell, January 4, 1912. Barometer during final record: max., 1.019; min., 0.988. Total daily pressures:

Preliminary Record

	Atms.		Atms.		Atms.
Jan. 5,	18.764	Jan. 7,	16.267	Jan. 9,	(not rec'd)
6,	17.088	8,	15.757		

Final Record

	Atms.		Atms.		Atms.
Jan. 10,	14.416	Jan. 14,	14.515	Jan. 17,	14.524
11,	14.451	15,	14.513	18,	14.518
12,	14.487	16,	14.520	19,	14.504
13,	14.499				(10 days)

Mean total pressure, Jan. 10–19 = 14.4947 atms.
Mean barom. pressure, Jan. 10–19 = 1.002 atms.
Mean osmot. pressure, Jan. 10–19 = 13.4927 atms.

Table LI

0.5 Wt. normal solution. Expt. 3 at 50°. Cell L_5. Resistance, 94,000 ohms. Manometer 9. Calc. gas pressure, 13.175 atms. Time of setting up cell, January 4, 1912. Barometer during final record: max., 1.019; min., 0.988. Total daily pressures:

Preliminary Record

			Atms.		
Jan. 5,	(not rec'd)	Jan. 7,	14.584	Jan. 9	(not rec'd)
6,	"	8,	14.500		

Final Record

	Atms.		Atms.		Atms.
Jan. 10,	14.435	Jan. 14,	14.526	Jan. 17,	14.518
11,	14.487	15,	14.511	18,	14.522
12,	14.522	16,	14.524	19,	14.508
13,	14.504				(10 days)

Mean total pressure, Jan. 10–19 = 14.5057 atms.
Mean barom. pressure, Jan. 10–19 = 1.002 atms.
Mean. osmot. pressure, Jan. 10–19 = 13.5037 atms.
Mean osmotic pressure for Expts. 1, 2 and 3 = 13.5037 atms.
Ratio of osmotic to gas pressure = 1.025

Table LII

0.5 Wt. normal solution. Expt. 1 at 60°. Cell V_5. Resistance, 11,600 ohms. Manometer 31. Calc. gas pressure, 13.584 atms. Time of setting up cell, Feb. 23, 1912. Barometer during final record: max., 1.018; min., 0.994. Total daily pressures:

Preliminary Record

	Atms.		Atms.		Atms.
Feb. 24,	19.002	Feb. 27,	16.210	Feb. 29,	14.852
25,	17.101	28,	15.059	Mar. 1,	14.730
26,	17.002				

Final Record

	Atms.		Atms.		Atms.
Mar. 2,	14.654	Mar. 6,	14.646	Mar. 10,	14.649
3,	14.654	7,	14.643	11,	14.654
4,	14.645	8,	14.688	12,	14.655
5,	14.634	9,	14.661		(11 days)

Mean total pressure, Mar. 2–12 = 14.653 atms.
Mean barom. pressure, Mar. 2–12 = 1.008 atms.
Mean osmot. pressure, Mar. 2–12 = 13.645 atms.

Table LIII

0.5 Wt. normal solution. Expt. 2 at 60°. Cell C_5. Resistance, 50,000 ohms. Manometer 4. Calc. gas pressure, 13.584 atms. Time of setting up cell, March 15, 1912. Barometer during final record: max., 1.014; min., 0.984. Total daily pressures:

Final Record

	Atms.		Atms.		Atms.
Mar. 18,	14.637	Mar. 22,	14.759	Mar. 25,	14.703
19,	14.608	23,	14.773	26,	14.707
20,	14.620	24,	14.724	27,	14.707
21,	14.635				(10 days)

Mean total pressure, Mar. 18–27 = 14.6873 atms.
Mean barom. pressure, Mar. 18–27 = 1.000 atm.
Mean osmot. pressure, Mar. 18–27 = 13.6873 atms.
Mean osmotic pressure for Expts. 1 and 2 = 13.662 atms.
Ratio of osmotic to gas pressure = 1.0057

Table LIV

0.5 Wt. normal solution. Expt. 1 at 70°. Cell E_5. Resistance, 13,000 ohms. Manometer 1. Calc. gas pressure, 13.992 atms. Time of setting up cell, May 13, 1912. Barometer during final record: max., 1.005; min., 0.982. Total daily pressures:

Final Record

	Atms.		Atms.		Atms.
May 16,	15.015	May 18,	14.985	May 20,	14.974
17,	14.986	19,	14.978		

Mean total pressure, May 16–20 = 14.988 atms.
Mean barom. pressure, May 16–20 = 0.994 atms.
Mean osmot. pressure, May 16–20 = 13.994 atms.

Table LV

0.5 Wt. normal solution. Expt. 2 at 70°. Cell L_5. Resistance, 9,600 ohms. Manometer 38. Calc. gas pressure, 13.992 atms. Time of setting up cell, May 13, 1912. Barometer during final record: max., 1.004; min., 0.982. Total daily pressures:

Final Record

	Atms.		Atms.		Atms.
May 15,	14.993	May 17,	14.981	May 19,	14.981
16,	14.984	18,	14.979	20,	14.985

Mean total pressure, May 15–20 = 14.984 atms.
Mean barom. pressure, May 15–20 = 0.994 atm.
Mean osmot. pressure, May 15–20 = 13.990 atms.
Mean osmotic pressure for Expts. 1 and 2 = 13.9905 atms.
Ratio of osmotic to gas pressure = 1.000

Table LVI

0.6 Wt. normal solution. Expt. 1 at 30°. Cell 105. Resistance, 250,000 ohms. Manometer 24. Calc. gas pressure, 14.830 atms. Time of setting up cell, Oct. 5, 1911. Barometer during final record: max., 1.008; min., 0.989. Total daily pressures:

Final Record

	Atms.		Atms.		Atms.
Oct. 7,	16.672	Oct. 10,	16.702	Oct. 12,	16.693
8,	16.771	11,	16.694	13,	16.699
9,	16.713				(7 days)

Mean total pressure, Oct. 7–13 = 16.706 atms.
Mean barom. pressure, Oct. 7–18 = 1.000 atm.
Mean osmot. pressure, Oct. 7–13 = 15.706 atms.

Table LVII

0.6 Wt. normal solution. Expt. 2 at 30°. Cell H_5. Reistance, 200,000 ohms. Manometer 15. Calc. gas pressure, 14.830 atms. Time of setting up cell, Oct. 5, 1911. Barometer during final record: max., 1.008; min., 0.993. Total daily pressures:

Final Record

	Atms.		Atms.		Atms.
Oct. 9,	16.733	Oct. 13,	16.688	Oct. 16,	16.691
10,	16.698	14,	16.683	17,	16.688
11,	16.691	15,	16.684	18,	16.688
12,	16.693				(10 days)

Mean total pressure, Oct. 9–18 = 16.6937 atms.
Mean barom. pressure, Oct. 9–18 = 1.000 atm.
Mean osmot. pressure, Oct. 9–18 = 15.6937 atms.

Table LVIII

0.6 Wt. normal solution. Expt. 3 at 30°. Cell 110. Resistance, 150,000 ohms. Manometer 29. Calc. gas pressure, 14.830 atms. Time of setting up cell, Oct. 5, 1911. Barometer during final record: max., 1.008; min., 0.993. Total daily pressures:

Final Record

	Atms.		Atms.		Atms.
Oct. 7,	16.734	Oct. 10,	16.772	Oct. 12,	16.752
8,	16.790	11,	16.760	13,	16.751
9,	16.782				(7 days)

Mean total pressure, Oct. 7–13 = 16.763 atms.
Mean barom. pressure, Oct. 7–13 = 1.000 atm.
Mean osmot. pressure, Oct. 7–13 = 15.763 atms.

Table LIX

0.6 Wt. normal solution. Expt. 4 at 30°. Cell B_5. Resistance, 200,000 ohms. Manometer 9. Calc. gas pressure, 14.830 atms. Time of setting up cell, Oct. 5, 1911. Barometer during final record: max., 1.008; min., 0.993. Total daily pressures:

Final Record

	Atms.		Atms.		Atms.
Oct. 10,	16.704	Oct. 12,	16.698	Oct. 13,	16.665
11,	16.693				

Mean total pressure, Oct. 10–13 = 16.690 atms.
Mean barom. pressure, Oct. 10–13 = 1.000 atm.
Mean osmot. pressure, Oct. 10–13 = 15.690 atms.
Mean osmotic pressure for Expts. 1, 2, 3 and 4 = 15.7132 atms.
Ratio of osmotic to gas pressure = 1.0595

Table LX

0.6 Wt. normal solution. Expt. 1 at 40°. Cell H_5. Resistance, 110,000 ohms. Manometer 6. Calc. gas pressure, 15.320 atms. Time of setting up cell, March 9, 1911. Barometer during final record: max., 1.009; min., 0.997. Total daily pressures:

Final Record

	Atms.		Atms.		Atms.
Mar. 11,	17.138	Mar. 13,	17.150	Mar. 14,	17.144
12,	17.153				(4 days)

Mean total pressure, Mar. 11–14 = 17.141 atms.
Mean barom. pressure, Mar. 11–14 = 1.004 atms.
Mean osmot. pressure, Mar. 11–14 = 16.137 atms.

Table LXI

0.6 Wt. normal solution. Expt. 2 at 40°. Cell E_5. Resistance, 110,000 ohms. Calc. gas pressure, 15.320 atms. Manometer 9. Time of setting up cell, March 9, 1911. Barometer during final record: max., 1.009; min., 0.997. Total daily pressures:

Final Record

	Atms.		Atms.		Atms.
Mar. 12,	17.150	Mar. 13,	17.159	Mar. 14,	17.161

Mean total pressure, Mar. 12–14 = 17.157 atms.
Mean barom. pressure, Mar. 12–14 = 1.003 atms.
Mean osmot. pressure, Mar. 12–14 = 16.154 atms.
Mean osmotic pressure for Expts. 1 and 2 = 16.146 atms.
Ratio of osmotic to gas pressure = 1.054

Table LXII

0.6 Wt. normal solution. Expt. 1 at 50°. Cell C_5. Resistance, 59,000 ohms. Manometer 31. Calc. gas pressure, 15.810 atms. Time of setting up cell, January 5, 1912. Barometer during final record: max., 1.019; min., 0.988. Total daily pressures:

Final Record

	Atms.		Atms.		Atms.
Jan. 10,	17.322	Jan. 15,	17.318	Jan. 19,	17.318
11,	17.339	16,	17.323	20,	17.320
12,	17.332	17,	17.318	21,	17.324
13,	17.333	18,	17.320	22,	17.320
14,	17.337				(13 days)

Mean total pressure, Jan. 10–22 = 17.325 atms.
Mean barom. pressure, Jan. 10–22 = 1.003 atms.
Mean osmot. pressure, Jan. 10–22 = 16.322 atms.

Table LXIII

0.6 Wt. normal solution. Expt. 2 at 50°. Cell R_5. Resistance, 118,000 ohms. Manometer 5. Calc. gas pressure, 15.810 atms. Time of setting up cell, January 5, 1912. Barometer during final record: max., 1.019; min., 0.988. Total daily pressures:

Preliminary Record

	Atms.		Atms.		Atms.
Jan. 6,	18.177	Jan. 8,	17.532	Jan. 10,	17.089
7,	18.742	9,	16.945	11,	17.172

Final Record

	Atms.		Atms.		Atms.
Jan. 12,	17.302	Jan. 16,	17.309	Jan. 20,	17.316
13,	17.296	17,	17.313	21,	17.313
14,	17.321	18,	17.302	22,	17.312
15,	17.313	19,	17.301		(11 days)

Mean total pressure, Jan. 12–22 = 17.309 atms.
Mean. barom. pressure, Jan. 12–22 = 1.003 atms.
Mean osmot. pressure, Jan. 12–22 = 16.306 atms.
Mean osmotic pressure for Expts. 1 and 2 = 16.319 atms.
Ratio of osmotic to gas pressure = 1.032

Table LXIV

0.6 Wt. normal solution. Expt. 1 at 60°. Cell R_5. Resistance, 29,000 ohms. Manometer 11. Calc. gas pressure, 16.300 atms. Time of setting up cell, March 6, 1912. Barometer during final record: max., 1.015; min., 0.985. Total daily pressures:

Preliminary Record

	Atms.		Atms.		Atms.
Mar. 7,	22.343	Mar. 9,	17.912	Mar. 11,	17.092
8,	19.050	10,	16.804	12,	17.343

Final Record

	Atms.		Atms.		Atms.
Mar. 13,	17.487	Mar. 16,	17.499	Mar. 19,	17.517
14,	17.498	17,	17.485	20,	17.546
15,	17.578	18,	17.522	21,	17.531

Mean total pressure, Mar. 13–21 = 17.518 atms.
Mean barom. pressure, Mar. 13–21 = 0.999 atm.
Mean osmot. pressure, Mar. 13–21 = 16.519 atms.

Table LXV

0.6 Wt. normal solution. Expt. 2 at 60°. Cell P_5. Resistance, 23,000 ohms. Manometer 5. Calc. gas pressure, 16.300 atms. Time of setting up cell, March 6, 1912. Barometer during final record: max., 1.015; min., 0.985. Total daily pressures:

Preliminary Record

	Atms.		Atms.		Atms.
Mar. 7,	18.627	Mar. 9,	17.301	Mar. 11,	17.262
8,	17.699	10,	16.454	12,	17.358

Final Record

	Atms.		Atms.		Atms.
Mar. 13,	17.555	Mar. 16,	17.553	Mar. 19,	17.527
14,	17.616	17,	17.523	20,	17.523
15,	17.585	18,	17.553	21,	17.519

Mean total pressure, Mar. 13–21 = 17.550 atms.
Mean. barom. pressure, Mar. 13–21 = 0.999 atm.
Mean osmot. pressure, Mar. 13–21 = 16.551 atms.
Mean osmotic pressure for Expts. 1 and 2 = 16.535 atms.
Ratio of osmotic to gas pressure = 1.014

Table LXVI

0.6 Wt. normal solution. Expt. 1 at 70°. Cell B_5. Resistance, 10,000 ohms. Manometer 31. Calc. gas pressure, 16.790 atms. Time of setting up cell, May 10, 1912. Barometer during final record: max., 1.002; min., 0.985. Total daily pressures:

Final Record

	Atms.		Atms.		Atms.
May 11,	17.812	May 13,	17.824	May 15,	17.800
12,	17.820	14,	17.816	16,	17.795

Mean total pressure, May 11–17 = 17.810 atms.
Mean barom. pressure, May 11–17 = 0.995 atm.
Mean osmot. pressure, May 11–17 = 16.815 atms.

Table LXVII

0.6 Wt. normal solution. Expt. 2 at 70°. Cell W_5. Resistance, 16,400 ohms. Manometer 15. Calc. gas pressure, 16.790 atms. Time of setting up cell, May 9, 1912. Barometer during final record: max., 1.004; min., 0.982. Total daily pressures:

Final Record

	Atms.		Atms.		Atms.
May 13,	17.859	May 15,	17.817	May 17	17.817
14,	17.822	16,	17.801	18,	17.800

Mean total pressure, May 13–18 = 17.819 atms.
Mean barom. pressure, May 13–18 = 0.995 atm.
Mean osmot. pressure, May 13–18 = 16.824 atms.
Mean osmotic pressure for Expts. 1 and 2 = 16.8195 atms.
Ratio of osmotic to gas pressure = 1.0018.

Table LXVIII

0.7 Wt. normal solution. Expt. 1 at 30°. Cell H_5. Resistance, 225,000 ohms. Manometer 24. Calc. gas pressure, 17.301 atms. Time of setting up cell, May 30, 1911. Barometer during final record: max., 1.004; min., 0.990. Total daily pressures:

Final Record

	Atms.		Atms.		Atms.
June 3,	19.505	June 7,	19.497	June 10,	19.483
4,	19.490	8,	19.497	11,	19.483
5,	19.487	9,	19.505	12,	19.483
6,	19.487			(10 days)	

Mean total pressure, June 3–12 = 19.4917 atms.
Mean barom. pressure, June 3–12 = 0.998 atm.
Mean osmot. pressure, June 3–12 = 18.4937 atms.

Table LXIX

0.7 Wt. normal solution. Expt. 2 at 30°. Cell B_5. Resistance, 110,000 ohms. Manometer 9. Calc. gas pressure, 17.301 atms. Time of setting up cell, June 3, 1911. Barometer during final record: max., 1.004; min., 0.990. Total daily pressures:

Final Record

	Atms.		Atms.		Atms
June 5,	19.524	June 8,	19.510	June 11,	19.482
6,	19.514	9,	19.496	12,	19.490
7,	19.507	10,	19.490		(8 days)

Mean total pressure, June 5–12 = 19.5016 atms.
Mean. barom. pressure, June 5–12 = 0.997 atm.
Mean osmot. pressure, June 5–12 = 18.5046 atms.
Mean osmotic pressure for Expts. 1 and 2 = 18.4992 atms.
Ratio of osmotic to gas pressure = 1.069

Table LXX

0.7 Wt. normal solution. Expt. 1 at 40°. Cell A_5. Resistance, 90,000 ohms. Manometer 6. Calc. gas pressure, 17.873 atms. Time of setting up cell, May 9, 1911. Barometer during final record: max., 1.005; min., 0.994. Total daily pressures:

Final Record

	Atms.		Atms.		Atms.
May 13,	19.943	May 15,	19.999	May 17,	19.960
14,	(not rec'd)	16,	19.956	18,	19.947

Mean total pressure, May 13–18 = 19.961 atms.
Mean barom. pressure, May 13–18 = 0.999 atm.
Mean osmot. pressure, May 13–18 = 18.962 atms.

Table LXXI

0.7 Wt. normal solution. Expt. 2 at 40°. Cell C_5. Resistance, 110,000 ohms. Manometer 24. Calc. gas pressure, 17.873 atms. Time of setting up cell, May 12, 1911. Barometer during final record: max., 1.010; min., 0.994. Total daily pressures:

Final Record

	Atms.		Atms.		Atms.
May 13,	19.934	May 15,	19.892	May 17,	19.900
14,	19.895	16,	19.887	18,	19.911

Mean total pressure, May 13–18 = 19.902 atms.
Mean barom. pressure, May 13–18 = 1.001 atms.
Mean osmot. pressure, May 13–18 = 18.901 atms.
Mean osmotic pressure for Expts. 1 and 2 = 18.932 atms.
Ratio of osmotic to gas pressure = 1.0592

Table LXXII

0.7 Wt. normal solution. Expt. 1 at 50°. Cell D_2. Resistance, 110,000 ohms. Manometer 29. Calc. gas pressure, 18.445 atms. Time of setting up cell, December 14, 1911. Barometer during final record: max., 1.003; min., 0.981. Total daily pressures:

Preliminary Record

	Atms.		Atms.		Atms.
Dec. 15,	25.092	Dec. 18,	22.417	Dec. 21,	20.464
16,	25.508	19,	21.285	22,	20.392
17,	23.246	20,	20.727		

Final Record

	Atms.		Atms.		Atms.
Dec. 23,	20.272	Dec. 25,	20.211	Dec. 27,	20.194
24,	20.237	26,	20.211	28,	20.198

Mean total pressure, Dec. 23–28 = 20.2205 atms.
Mean barom pressure, Dec. 23–28 = 0.996 atm.
Mean osmot. pressure, Dec. 23–28 = 19.2245 atms.

Table LXXIII

0.7 Wt. normal solution. Expt. 2 at 50°. Cell Z_3. Resistance, 150,000 ohms. Manometer 4. Calc. gas pressure, 18.445 atms. Time of setting up cell, December 14, 1911. Barometer during final record: max., 1.003; min., 0.981. Total daily pressures:

Preliminary Record

	Atms.		Atms.		Atms.
Dec. 16,	21.728	Dec. 18,	20.601	Dec. 20,	19.652
17,	20.597	19,	19.554	21,	19.869

Final Record

	Atms.		Atms.		Atms.
Dec. 22,	20.297	Dec. 25,	20.178	Dec. 27,	20.143
23,	20.103	26,	20.164	28,	20.164
24,	20.186				

Mean total pressure, Dec. 22–28 = 20.1764 atms.
Mean barom. pressure, Dec. 22–28 = 0.997 atm.
Mean osmot. pressure, Dec. 22–28 = 19.1794 atms.
Mean osmotic pressure for Expts. 1 amd 2 = 19.2019 atms.
Ratio of osmotic to gas pressure = 1.041

Table LXXIV

0.7 Wt. normal solution. Expt. 1 at 60°. Cell Z_5. Resistance, 27,-ohms. Manometer 39. Calc. gas pressure, 19.017 atms. Time of setting up cell, March 14, 1912. Barometer during final record: max., 1.014; min., 0.984. Total daily pressures:

Final Record

	Atms.		Atms.		Atms.
Mar. 19,	20.319	Mar. 23,	20.450	Mar. 26,	20.438
20,	20.357	24,	20.444	27,	20.426
21,	20.362	25,	20.441	28,	20.410
22,	20.371				(10 days)

Mean total pressure, March 19–28 = 20.4018 atms.
Mean barom. pressure, March 19–28 = 0.999 atm.
Mean osmot. pressure, March 19–28 = 19.4028 atms.

Table LXXV

0.7 Wt. normal solution. Expt. 2 at 60°. Cell A_5. Resistance, 58,000 ohms. Manometer 31. Calc. gas pressure, 19.017 atms. Time of setting up cell, March 14, 1912. Barometer during final record: max., 1.014; min., 0.974. Total daily pressures:

Preliminary Record

	Atms.		Atms.		Atms.
Mar. 15,	24.111	Mar. 18,	21.524	Mar. 20,	20.770
16,	23.161	19,	21.118	21,	20.552
17,	21.879				(7 days)

Final Record

	Atms.		Atms.		Atms.
Mar. 22,	20.428	Mar. 26,	20.400	Mar. 30,	20.395
23,	20.409	27,	20.390	31,	20.395
24,	20.417	28,	20.400	Apr. 1,	20.395
25,	20.416	29,	20.395		(11 days)

Mean total pressure, March 22–April 1 = 20.4036 atms.
Mean barom. pressure, March 22–April 1 = 0.999 atm.
Mean osmot. pressure, March 22–April 1 = 19.4046 atms.
Mean osmotic pressure for Expts. 1 and 2 = 19.4037 atms.
Ratio of osmotic to gas pressure = 1.020

Table LXXVI

0.7 Wt. normal solution. Expt. 1 at 70°. Cell J_5. Resistance, 8,000 ohms. Manometer 38. Calc. gas pressure, 19.587 atms. Time of setting up cell, May 2, 1912. Barometer during final record: max., 0.998; min., 0.984. Total daily pressures:

Preliminary Record

	Atms.		Atms.		Atms.
May 3,	19.933	May 5,	20.154	May 7,	20.035
4,	21.154	6,	20.446		

Final Record

	Atms.		Atms.		Atms.
May 8,	20.557	May 10,	20.516	May 12,	20.528
9,	20.564	11,	20.516	13,	20.534

Mean total pressure, May 8–13 = 20.543 atms.
Mean barom. pressure, May 8–13 = 0.990 atms.
Mean osmot. pressure, May 8–13 = 19.553 atms.

Table LXXVII

0.7 Wt. normal solution. Expt. 2 at 70°. Cell F_5. Resistance, 10,000 ohms. Manometer 24. Calc. gas pressure, 19.589 atms. Time of setting up cell, May 11, 1912. Barometer during final record: max., 1.004; min., 0.982. Total daily pressures:

Final Record

	Atms.		Atms.		Atms.
May 13,	20.559	May 15,	20.600	May 17,	20.578
14,	20.574	16,	20.592	18,	20.566

Mean total pressure, May 13–18 = 20.577 atms.
Mean barom. pressure, May 13–18 = 0.994 atm.
Mean osmot. pressure, May 13–18 = 19.583 atms.
Mean osmotic pressure for Expts. 1 and 2 = 19.568 atms.
Ratio of osmotic to gas pressure = 0.999

Table LXXVIII

0.8 Wt. normal solution. Expt. 1 at 30°. Cell C_5. Resistance, 220,000 ohms. Manometer 29. Calc. gas pressure, 19.773 atms. Time of setting up cell, May 26, 1911. Barometer during final record: max., 1.002; min., 0.989. Total daily pressures:

Final Record

	Atms.		Atms.		Atms.
May 29,	22.421	May 31,	22.392	June 2,	22.381
30,	22.392	June 1,	22.396	3,	22.387

Mean total pressure, May 29–June 3 = 22.395 atms.
Mean barom. pressure, May 29–June 3 = 0.999 atm.
Mean osmot. pressure, May 29–June 3 = 21.396 atms.

Table LXXIX

0.8 Wt. normal solution. Expt. 2 at 30°. Cell A_5. Resistance, 110,000 ohms. Manometer 9. Calc. gas pressure, 19.773 atms. Time of setting up cell, May 26, 1911. Barometer during final record: max., 1.003; min., 0.989.

Final Record

	Atms.		Atms.		Atms.
May 28,	22.389	May 31,	22.347	June 2,	22.342
29,	22.361	June 1,	22.342	3,	22.352
30,	22.339				

Mean total pressure, May 28–June 3 = 22.353 atms.
Mean barom. pressure, May 28–June 3 = 0.999 atm.
Mean osmot. pressure, May 28–June 3 = 21.354 atms.
Mean osmotic pressure for Expts. 1 and 2 = 21.375 atms.
Ratio of osmotic to gas pressure = 1.081

Table LXXX

0.8 Wt. normal solution. Expt. 1 at 40°. Cell I_5. Resistance, 100,000 ohms. Manometer 5. Calc. gas pressure, 20.426 atms. Time of setting up cell, February 23, 1911. Barometer during final record: max., 1.009; min., 0.988. Total daily pressures:

Final Record

	Atms.		Atms.		Atms.
Feb. 27,	22.779	Mar. 1,	22.780	Mar. 2,	22.767
28,	22.788				

Mean total pressure, Feb. 27–Mar. 2 = 22.779 atms.
Mean barom. pressure, Feb. 27–Mar. 2 = 1.000 atm.
Mean osmot. pressure, Feb. 27–Mar. 2 = 21.779 atms.

Table LXXXI

0.8 Wt. normal solution. Expt. 2 at 40°. Cell A_5. Resistance, 225,000 ohms. Manometer 9. Calc. gas pressure, 20.426 atms. Time of setting up cell, March 3, 1911. Barometer during final record: max., 1.016; min., 1.006. Total daily pressures:

Final Record

	Atms.		Atms.		Atms.
Mar. 7,	22.831	Mar. 8,	22.817	Mar. 9,	22.822

Mean total pressure, Mar. 7–9 = 22.823 atms.
Mean barom. pressure, Mar. 7–9 = 1.010 atms.
Mean osmot. pressure, Mar. 7–9 = 21.813 atms.

Table LXXXII

0.8 Wt. normal solution. Expt. 3 at 40°. Cell B_5. Resistance, 220,000 ohms. Manometer 6. Calc. gas pressure, 20.426 atms. Time of setting up cell, March 3, 1911. Barometer during final record: max., 1.016; min., 0.999. Total daily pressures:

Final Record

	Atms.		Atms.		Atms.
Mar. 4,	22.859	Mar. 6,	22.842	Mar. 8,	22.842
5,	22.768	7,	22.813	9,	22.836

Meam total pressure, Mar. 4–9 = 22.827 atms.
Mean barom. pressure, Mar. 4–9 = 1.008 atms.
Mean osmot. pressure, Mar. 4–9 = 22.819 atms.

Table LXXXIII

0.8 Wt. normal solution. Expt. 4 at 40°. Cell D_5. Resistance, 333,000 ohms. Manometer 22. Calc. gas pressure, 20.426 atms. Time of setting up cell, March 3, 1911. Barometer during final record: max., 1.018; min., 0.999. Total daily pressures:

Final Record

	Atms.		Atms.		Atms.
Mar. 4,	22.788	Mar. 6,	22.823	Mar. 8,	22.836
5,	22.800	7,	22.845	9,	22.829

Mean total pressure, March 4–9 = 22.820 atms.
Mean barom. pressure, March 4–9 = 1.009 atms.
Mean osmot. pressure, March 4–9 = 21.811 atms.
Mean osmotic pressure for Expts. 1, 2, 3 and 4 = 21.8028 atms.
Ratio of osmotic to gas pressure = 1.0674

Table LXXXIV

0.8 Wt. normal soln. Expt. 1 at 50°. Cell C_5. Resistance, 110,000 ohms. Manometer 28. Calc. gas pressure, 21.080 atms. Time of setting up cell, December 12, 1911. Barometer during final record: max., 1.014; min., 0.989. Total daily pressures:

Final Record

	Atms.		Atms.		Atms.
Dec. 13,	23.095	Dec. 18,	23.146	Dec. 23,	21.115
14,	23.116	19,	23.146	24,	23.075
15,	23.180	20,	23.158	25,	23.095
16,	23.164	21,	23.165	26,	23.115
17,	23.164	22,	23.135		(14 days)

Mean total pressure, Dec. 13–26 = 23.1335 atms.
Mean barom. pressure, Dec. 13–26 = 1.005 atms.
Mean osmot. pressure, Dec. 13–26 = 22.1285 atms.

Table LXXXV

0.8 Wt. normal solution. Expt. 2 at 50°. Cell J_5. Resistance, 100,000 ohms. Manometer 31. Calc. gas pressure, 21.080 atms. Time of setting up cell, December 12, 1911. Barometer during final record: max., 1.014; min., 0.989. Total daily pressures:

Final Record

	Atms.		Atms.		Atms.
Dec. 15,	23.069	Dec. 20,	23.149	Dec. 24,	23.103
16,	23.079	21,	23.131	25,	23.118
17,	23.068	22,	23.122	26,	23.107
18,	23.102	23,	23.107		
19,	23.135				(12 days)

Mean total pressure, Dec. 15–26 = 23.1075 atms.
Mean barom. pressure, Dec. 15–26 = 1.004 atms.
Mean osmot. pressure, Dec. 15–26 = 22.1035 atms.
Mean osmotic pressure for Expts. 1 and 2 = 22.116 atms.
Ratio of osmotic to gas pressure = 1.049.

Table LXXXVI

0.8 Wt. normal solution. Expt. 1 at 60°. Cell P_5. Resistance, 25,000 ohms. Manometer 1. Calc. gas pressure, 21.734 atms. Time of setting up cell, March 26, 1912. Barometer during final record: max., 1.012; min., 0.977. Total daily pressures:

Final Record

	Atms.		Atms.		Atms.
Mar. 28,	23.358	Apr. 1,	23.345	Apr. 5,	23.348
29,	23.339	2,	23.339	6,	23.339
30,	23.348	3,	23.318	7,	23.325
31,	23.348	4,	23.357	8,	23.339
					(12 days)

Mean total pressure, Mar. 28–Apr. 8 = 23.342 atms.
Mean barom. pressure, Mar. 28–Apr. 8 = 0.998 atm.
Mean osmot. pressure, Mar. 28–Apr. 8 = 22.344 atms.

Table LXXXVII

0.8 Wt. normal solution. Expt. 2 at 60°. Cell E_5. Resistance, 20,000 ohms. Manometer 15. Calc. gas pressure, 21.734 atms. Time of setting up cell, March 26, 1912. Barometer during final record: max., 1.012; min., 0.977. Total daily pressures:

Final Record

	Atms.		Atms.		Atms.
Mar. 30,	23.291	Apr. 3,	23.286	Apr. 7,	23.257
31,	(not rec'd)	4,	23.312	8,	23.349
Apr. 1,	23.329	5,	23.276	9,	23.345
2,	23.316	6,	23.298	10,	23.323
					(12 days)

Mean total pressure, March 30–April 10 = 23.308 atms.
Mean barom. pressure, March 30–April 10 = 0.998 atm.
Mean. osmot. pressure, March 30–April 10 = 22.310 atms.
Mean osmotic pressure for Expts. 1 and 2 = 22.327 atms.
Ratio of osmotic to gas pressure = 1.027

Table LXXXVIII

0.8 Wt. normal solution. Expt. 1 at 70°. Cell U_5. Resistance, 23,000 ohms. Manometer 31. Calc. gas pressure, 22.387 atms. Time of setting up cell, April 29, 1912. Barometer during final record: max., 0.998; min., 0.984. Total daily pressures:

Preliminary Record

	Atms.		Atms.		Atms.
Apr. 30,	25.575	May 2,	24.047	May 4,	23.628
May 1,	24.159	3,	23.810		

Final Record

May 5,	23.555	May 7,	23.547	May 9,	23.574
6,	23.549	8,	23.562	10,	23.568

Mean total pressure, May 5–10 = 23.559 atms.
Mean barom. pressure, May 5–10 = 0.992 atm.
Mean osmot. pressure, May 5–10 = 22.567 atms.

Table LXXXIX

0.8 Wt. normal solution. Expt. 2 at 70°. Cell R_5. Resistance, 10,000 ohms. Manometer 31. Calc. gas pressure, 22.387 atms. Time of setting up cell, May 16, 1912. Barometer during final record: max., 1.005; min., 1.001. Total daily pressures:

Final Record

	Atms.		Atms.		Atms.
May 18,	23.568	May 20,	23.556	May 22,	23.576
19,	23.565	21,	23.583		

Mean total pressure, May 18–22 = 23.570 atms.
Mean barom. pressure, May 18–22 = 1.003 atms.
Mean osmot. pressure, May 18–22 = 22.567 atms.
Mean osmotic pressure for Expts. 1 and 2 = 22.567 atms.
Ratio of osmotic to gas pressure = 1.008

Table XC

0.8 Wt. normal solution. Expt. 1 at 80°. Cell B_5. Resistance, 9,000 ohms. Manometer 24. Calc. gas pressure, 23.041 atms. Time of setting up cell, May 18, 1912. Barometer during final record: max., 1.004; min., 0.991. Total daily pressures:

Final Record

	Atms.		Atms.		Atms.
May 22,	24.087	May 24,	24.042	May 25,	24.036
23,	24.073				

Mean total pressure, May 22–25 = 24.060 atms.
Mean barom. pressure, May 22–25 = 0.998 atm.
Mean osmot. pressure, May 22–25 = 23.062 atms.
Ratio of osmotic to gas pressure = 1.001

Table XCI

0.9 Wt. normal solution. Expt. 1 at 30°. Cell Z_3. Resistance, 250,000 ohms. Manometer 15. Calc. gas pressure, 22.244 atms. Time of setting up cell, October 29, 1910. Barometer during final record: max., 1.001; min., 0.991. Total daily pressures:

Final Record

	Atms.		Atms.		Atms.
Nov. 2,	25.249	Nov. 4,	(not rec'd)	Nov. 6,	25.194
3,	25.198	5,	25.214	7,	25.193

Mean total pressure, Nov. 2–7 = 25.2096 atms.
Mean barom. pressure, Nov. 2–7 = 0.995 atm.
Mean osmot. pressure, Nov. 2–7 = 24.2146 atms.

Table XCII

0.9 Wt. normal solution. Expt. 2 at 30°. Cell Co_1. Resistance of membrane (cobalt ferrocyanide), 240,000 ohms. Manometer 24. Calc. gas pressure, 22.244 atms. Time of setting up cell, May 24, 1911. Barometer during final record: max., 1.002; min., 0.997. Total daily pressures:

Final Record

	Atms.		Atms.		Atms.
May 26,	25.246	May 28,	25.245	May 30,	25.245
27,	25.227	29,	25.220	31,	25.245

Mean total pressure, May 26–31 = 25.238 atms.
Mean barom. pressure, May 26–31 = 1.000 atm.
Mean osmot. pressure, May 26–31 = 24.238 atms.
Mean osmotic pressure for Expts. 1 and 2 = 24.2263 atms.
Ratio of osmotic to gas pressure = 1.089

Table XCIII

0.9 Wt. normal solution. Expt. 1 at 40°. Cell Ni_3. Resistance of membrane (nickel ferrocyanide), 80,000 ohms. Manometer 29. Calc. gas pressure, 22.980 atms. Time of setting up cell, May 1, 1911. Barometer during final record: max., 1.010; min., 0.991. Total daily pressures:

Preliminary Record

	Atms.		Atms.		Atms.
May 2,3,4,	(not rec'd)	May 8,	25.932	May 11,	25.477
5,	27.950	9,	(not rec'd)	12,	25.477
6,	26.336	10,	25.466	13,	25.582
7,	25.975				

Final Record

	Atms.		Atms.		Atms.
May 14,	25.701	May 16,	25.740	May 18,	25.743
15,	25.745	17,	25.737	19,	25.748

Mean total pressure, May 14–19 = 25.738 atms.
Mean barom. pressure, May 14–19 = 1.000 atm.
Mean osmot. pressure, May 14–19 = 24.738 atms.

Table XCIV

0.9 Wt. normal solution. Expt. 2 at 40°. Cell H_5. Resistance, 80,000 ohms. Manometer 9. Calc gas pressure, 22.980 atms. Time of setting up cell, May 1, 1911. Barometer during final record: max., 1.010; min., 0.986. Total daily pressures:

Final Record

	Atms.		Atms.		Atms.
May 4,	25.738	May 6,	25.751	May 8,	25.726
5,	25.720	7,	25.707	9,	25.745

Mean total pressure, May 4–9 = 25.731 atms.
Mean barom. pressure, May 4–9 = 1.001 atms.
Mean osmot. pressure, May 4–9 = 24.730 atms.

Table XCV

0.9 Wt. normal solution. Expt. 3 at 40°. Cell R_3. Resistance, 125,000 ohms. Manometer 22. Calc. gas pressure, 22.980 atms. Time of setting up cell, May 9, 1911. Barometer during final record: max., 1.010; min., 0.991. Total daily pressures:

Final Record

	Atms.		Atms.		Atms.
May 14,	25.710	May 16,	25.718	May 18,	25.741
15,	25.763	17,	25.733	19,	25.761

Mean total pressure, May 14–19 = 25.738 atms.
Mean barom. pressure, May 14–19 = 1.000 atm.
Mean osmot. pressure, May 14–19 = 24.738 atms.
Mean osmotic pressure for Expts. 1, 2 and 3 = 24.735 atms.
Ratio of osmotic to gas pressure = 1.076

Table XCVI

0.9 Wt. normal solution. Expt. 1 at 50°. Cell G_5. Resistance, 100,000 ohms. Manometer 1. Calc. gas pressure, 23.715 atms. Time of setting up cell, November 22, 1911. Barometer during final record: max., 1.013; min., 0.984. Total daily pressures:

Final Record

	Atms.		Atms.		Atms.
Nov. 26,	26.103	Nov. 30,	26.115	Dec. 3,	26.127
27,	26.127	Dec. 1,	26.139	4,	26.150
28,	26.133	2,	26.161	5,	26.139
29,	26.127				(10 days)

Mean total pressure, Nov. 26–Dec. 5 = 26.132 atms.
Mean barom. pressure, Nov. 26–Dec. 5 = 1.000 atm.
Mean osmot. pressure, Nov. 26–Dec. 5 = 25.132 atms.

Table XCVII

0.9 Wt. normal solution. Expt. 2 at 50°. Cell F_3. Resistance, 100,000 ohms. Manometer 38. Calc. gas pressure, 23.715 atms. Time of setting up cell, Nov. 22, 1911. Barometer during final record: max., 1.013; min., 0.984. Total daily pressures:

Final Record

	Atms.		Atms.		Atms.
Nov. 26,	26.128	Nov. 30,	26.108	Dec. 3,	26.105
27,	26.142	Dec. 1,	26.082	4,	26.107
28,	26.127	2,	26.105	5,	26.108
29,	26.124				(10 days)

Mean total pressure, Nov. 26–Dec. 5 = 26.1136 atms.
Mean barom. pressure, Nov. 26–Dec. 5 = 1.000 atm.
Mean osmot. pressure, Nov. 26–Dec. 5 = 25.1136 atms.
Mean osmotic pressure for Expts. 1 and 2 = 25.1228 atms.
Ratio of osmotic to gas pressure = 1.0593

Table XCVIII

0.9 Wt. normal solution. Expt. 1 at 60°. Cell G_3. Resistance, 38,000 ohms. Manometer 28. Calc. gas pressure, 24.450 atms. Time of setting up cell, March 11, 1912. Barometer during final record: max., 1.014; min., 0.984. Total daily pressures:

Preliminary Record

	Atms.		Atms.		Atms.
Mar. 12,	33.353	Mar. 16,	25.902	Mar. 19,	25.856
13,	28.555	17,	25.753	20,	25.848
14,	26.730	18,	25.887	21,	25.850
15,	25.968				(10 days)

Final Record

	Atms.		Atms.		Atms.
Mar. 22,	26.208	Mar. 26,	26.260	Mar. 30,	26.269
23,	26.225	27,	26.262	31,	26.269
24,	26.237	28,	26.264	Apr. 1,	26.283
25,	26.250	29,	26.271		(11 days)

Mean total pressure, Mar. 22–Apr. 1 = 26.2544 atms.
Mean. barom. pressure, Mar. 22–Apr. 1 = 0.998 atm.
Mean osmot. pressure, Mar. 22–Apr. 1 = 25.2564 atms.

Table XCIX

0.9 Wt. normal solution. Expt. 2 at 60°. Cell U_5. Resistance, 23,000 ohms. Manometer 5. Calc. gas pressure, 24.450 atms. Time of setting up cell, March 18, 1912. Barometer during final record: max., 1.014; min., 0.984. Total daily pressures:

Final Record

	Atms.		Atms.		Atms.
Mar. 22,	26.234	Mar. 26,	26.276	Mar. 30,	26.281
23,	26.234	27,	26.287	31,	26.321
24,	26.234	28,	26.283	Apr. 1,	26.342
25,	26.256	29,	26.276		(11 days)

Mean total pressure, Mar. 22–Apr. 1 = 26.274 atms.
Mean barom. pressure, Mar. 22–Apr. 1 = 0.999 atm.
Mean osmot. pressure, Mar. 22–Apr. 1 = 25.275 atms.
Mean osmotic pressure for Expts. 1 and 2 = 25.2657 atms.
Ratio of osmotic to gas pressure = 1.0334

Table C

0.9 Wt. normal solution. Expt. 1 at 70°. Cell F_5. Resistance, 19,100 ohms. Manometer 24. Calc. gas pressure, 25.186 atms. Time of setting up cell, April 19, 1912. Barometer during final record: max., 1.016; min., 0.984. Total daily pressures:

Preliminary Record

	Atms.		Atms.		Atms.
Apr. 20,	28.709	Apr. 24,	26.145	Apr. 28,	(not rec.)
21,	26.273	25,	26.113	29,	27.671
22,	26.689	26,	26.312	30,	27.040
23,	26.137	27,	27.688		(11 days)

Final Record

	Atms.		Atms.		Atms.
May 1,	26.543	May 4,	26.562	May 6,	26.549
2,	26.593	5,	26.523	7,	26.574
3,	26.556				(7 days)

Mean total pressure, May 1–7 = 26.557 atms.
Mean barom. pressure, May 1–7 = 0.998 atm.
Mean. osmot. pressure, May 1–7 = 25.559 atms.

Table CI

0.9 Wt. normal solution. Expt. 2 at 70°. Cell R_5. Resistance, 16,500 ohms. Manometer 28. Calc. gas pressure, 25.186 atms. Time of setting up cell, April 29, 1912. Barometer during final record: max., 1.002; min., 0.989. Total daily pressures:

Final Record

	Atms.		Atms.		Atms.
May 3,	26.589	May 5,	26.565	May 7,	26.551
4,	26.590	6,	26.559		(5 days)

Mean total pressure, May 3–7 = 26.571 atms.
Mean barom. pressure, May 3–7 = 0.997 atm.
Mean osmot. pressure, May 3–7 = 25.574 atms.

Table CII

0.9 Wt. normal solution. Expt. 3 at 70°. Cell C_5. Resistance, 7,700 ohms. Manometer 1. Calc. gas pressure, 25.186 atms. Time of setting up cell, April 29, 1912. Barometer during final record: max., 1.002; min., 0.989. Total daily pressures:

Final Record

	Atms.		Atms.		Atms.
May 2,	26.552	May 4,	26.552	May 6,	26.563
3,	26.534	5,	25.564	7,	26.541

Mean total pressure, May 2–7 = 26.551 atms.
Mean barom. pressure, May 2–7 = 0.997 atms.
Mean osmot. pressure, May 2–7 = 25.554 atms.
Mean osmot. pressure for Expts. 1, 2 and 3 = 25.562 atms.
Ratio of osmotic to gas pressure = 1.015

Table CIII

0.9 Wt. normal solution. Expt. 1 at 80°. Cell E_5. Resistance, 10,000 ohms. Manometer 31. Calc. gas pressure, 25.921 atms. Time of setting up cell, May 23, 1912. Barometer during final record: max., 1.001; min., 0.991. Total daily pressures:

Final Record

	Atms.		Atms.		Atms.
May 24,	26.905	May 26,	26.914	May 27,	26.919
25,	26.909				

Mean total pressure, May 24–27 = 26.912 atms.
Mean barom. pressure, May 24–27 = 0.997 atm.
Mean osmot. pressure, May 24–27 = 25.915 atms.

Table CIV

0.9 Wt. normal solution. Expt. 2 at 80°. Cell G_5. Resistance, 10,000 ohms. Manometer 5. Calc. gas pressure, 25.921 atms. Time of setting up cell, May 20, 1912. Barometer during final record: max., 1.001; min., 0.991. Total daily pressures:

Final Record

	Atms.		Atms.		Atms.
May 23,	26.974	May 25,	26.909	May 27,	26.909
24,	26.933	26,	26.873		

Mean total pressure, May 23–27 = 26.920 atms.
Mean barom. pressure, May 23–27 = 0.998 atm.
Mean osmot. pressure, May 23–27 = 25.922 atms.
Mean osmotic pressure for Expts. 1 and 2 = 25.919 atms.
Ratio of osmotic to gas pressure = 1.000

Table CV

1.0 Wt. normal solution. Expt. 1 at 30°. Cell R_5. Resistance, 110,000 ohms. Manometer 9. Calc. gas pressure, 24.716 atms. Time of setting up cell, May 4, 1910. Barometer during final record: max., 0.998; min., 0.991. Total daily pressures:

Final Record

	Atms.		Atms.		Atms.
May 7,	28.317	May 8,	28.206	May 9,	28.186

Mean total pressure, May 7–9 = 28.236 atms.
Mean barom. pressure, May 7–9 = 0.996 atm.
Mean osmot. pressure, May 7–9 = 27.240 atms.

Table CVI

1.0 Wt. normal solution. Expt. 2 at 30°. Cell Z_5. Resistance, 300,000 ohms. Manometer 9. Calc. gas pressure, 24.716 atms. Time of setting up cell, May 11, 1910. Barometer during final record: max., 1.011; min., 0.993. Total daily pressures:

Final Record

	Atms.		Atms.		Atms.
May 12,	28.219	May 15,	28.227	May 17,	28.212
13,	28.212	16,	28.206	18,	28.227
14,	28.212				

Mean total pressure, May 12–18 = 28.2164 atms.
Mean barom. pressure, May 12–18 = 1.001 atms.
Mean osmot. pressure, May 12–18 = 27.2154 atms.

Table CVII

1.0 Wt. normal solution. Expt. 3 at 30°. Cell F_5. Resistance, 147,000 ohms. Manometer 9. Calc. gas pressure, 24.716 atms. Time of setting up cell, May 18, 1910. Barometer during final record: max., 1.000; min., 0.992. Total daily pressures:

Final Record

	Atms.		Atms.		Atms.
May 19,	28.227	May 21,	28.250	May 23,	28.242
20,	28.234	22,	28.242		

Mean total pressure, May 19–23 = 28.239 atms.
Mean barom. pressure, May 19–23 = 0.996 atm.
Mean osmot. pressure, May 19–23 = 27.242 atms.

Table CVIII

1.0 Wt. normal solution. Expt. 4 at 30°. Cell G_5. Resistance, 140,000 ohms. Manometer 15. Calc. gas pressure, 24.716 atms. Time of setting up cell, December 13, 1910. Barometer during final record: max., 1.012; min., 0.987. Total daily pressures:

Final Record

	Atms.		Atms.		Atms.
Dec. 15,	28.205	Dec. 16,	28.215	Dec. 17,	28.192

Mean total pressure, Dec. 15–17 = 28.203 atms.
Mean barom. pressure, Dec. 15–17 = 1.007 atms.
Mean osmot. pressure, Dec. 15–17 = 27.196 atms.
Mean osmotic pressure for Expts. 1, 2, 3 and 4 = 27.2234 atms.
Ratio of osmotic to gas pressure = 1.101

Table CIX

1.0 Wt. normal solution. Expt. 1 at 40°. Cell B_5. Resistance, 150,000 ohms. Manometer 20. Calc. gas pressure, 25.533 atms. Time of setting up cell, March 9, 1910. Barometer during final record: max., 1.005; min., 0.996. Total daily pressures:

Final Record

	Atms.		Atms.		Atms.
Mar. 10,	28.697	Mar. 11,	28.641	Mar. 12,	28.687

Mean total pressure, Mar. 10–12 = 28.675 atms.
Mean barom. pressure, Mar. 10–12 = 1.002 atms.
Mean osmot. pressure, Mar. 10–12 = 27.673 atms.

Table CX

1.0 Wt. normal solution. Expt. 2 at 40°. Cell R_3. Resistance, 110,000 ohms. Manometer 9. Calc. gas pressure, 25.533 atms. Time of setting up cell, June 3, 1910. Barometer during final record: max., 1.004; min., 0.992. Total daily pressures:

Final Record

	Atms.		Atms.		Atms.
June 5,	28.785	June 7,	28.732	June 9,	28.725
6,	28.739	8,	28.732	10,	28.732

Mean total pressure, June 5–10 = 28.741 atms.
Mean barom. pressure, June 5–10 = 0.998 atm.
Mean osmot. pressure, June 5–10 = 17.743 atms.

Table CXI

1.0 Wt. normal solution. Expt. 3 at 40°. Cell F_3. Resistance, 112,000 ohms. Manometer 5. Calc. gas pressure, 25.533 atms. Time of setting up cell, January 27, 1911. Barometer during final record: max., 1.008; min., 0.987. Total daily pressures:

Final Record

	Atms.		Atms.		Atms.
Feb. 1,	28.695	Feb. 3,	28.684	Feb. 4,	28.721
2,	28.639				

Mean total pressure, Feb. 1–4 = 28.685 atms.
Mean barom. pressure, Feb. 1–4 = 0.997 atm.
Mean osmot. pressure, Feb. 1–4 = 27.688 atms.
Mean osmotic pressure for Expts. 1, 2 and 3 = 27.701 atms.
Ratio of osmotic to gas pressure = 1.085.

Table CXII

1.0 Wt. normal solution. Expt. 1 at 50°. Cell R_3. Resistance, 55,000 ohms. Manometer 9. Calc. gas pressure, 26.350 atms. Time of setting up cell, June 17, 1910. Barometer during final record: max., 0.996; min., 0.991. Total daily pressures:

Final Record

	Atms.		Atms.		Atms.
June 18,	29.194	June 21,	29.178	June 23,	29.230
19,	29.177	22,	29.193	24,	29.194
20,	29.186				

Mean total pressure, June 18–24 = 29.193 atms.
Mean barom. pressure, June 18–24 = 0.994 atm.
Mean osmot. pressure, June 18–24 = 28.199 atms.

Table CXIII

1.0 Wt. normal solution. Expt. 2 at 50°. Cell P_5. Resistance, 110,000 ohms. Manometer 29. Calc. gas pressure, 26.350 atms. Time of setting up cell, November 15, 1911. Barometer during final record: max., 1.008; min., 0.977. Total daily pressures:

Final Record

	Atms.		Atms.		Atms.
Nov. 17,	29.230	Nov. 21,	29.225	Nov. 25,	29.213
18,	29.228	22,	29.221	26,	29.209
19,	29.250	23,	29.240	27,	29.213
20,	29.236	24,	29.243		(11 days)

Mean total pressure, Nov. 17–27 = 29.228 atms.

Mean. barom. pressure, Nov. 17–27 = 0.997 atm.

Mean osmot. pressure, Nov. 17–27 = 28.231 atms.

Table CXIV

1.0 Wt. normal solution. Expt. 3 at 50°. Cell E_5. Resistance, 62,000 ohms. Manometer 5. Calc. gas pressure, 26.350 atms. Time of setting up cell, November 18, 1911. Barometer during final record: max., 1.008; min., 0.984. Total daily pressures:

Final Record

	Atms.		Atms.		Atms.
Nov. 23,	29.130	Nov. 27,	29.218	Dec. 1,	29.224
24,	29.153	28,	29.211	2,	29.211
25,	29.164	29,	29.218	3,	29.211
26,	29.150	30,	29.164	4,	29.224
					(12 days)

Mean total pressure, Nov. 23–Dec. 4 = 29.190 atms.

Mean barom. pressure, Nov. 23–Dec. 4 = 0.994 atm.

Mean osmot. pressure, Nov. 23–Dec. 4 = 28.196 atms.

Mean osmotic pressure for Expts. 1, 2 and 3 = 28.213 atms.

Ratio of osmotic to gas pressure = 1.071

Table CXV

1.0 Wt. normal solution. Expt. 1 at 60°. Cell W_5. Resistance, 3,200 ohms. Manometer 11. Calc. gas pressure, 27.167 atms. Time of setting up cell, March 21, 1911. Barometer during final record: max., 1.005; min., 0.977. Total daily pressures:

Final Record

	Atms.		Atms.		Atms.
Mar. 24,	29.358	Mar. 28,	29.339	Mar. 31,	29.371
25,	29.298	29,	29.371	Apr. 1,	29.380
26,	29.309	30,	29.439	2,	29.358
27,	29.282				(10 days)

Mean total pressure, Mar. 24–Apr. 2 = 29.351 atms.

Mean barom. pressure, Mar. 24–Apr. 2 = 0.994 atm.

Mean osmot. pressure, Mar. 24–Apr. 2 = 28.357 atms.

Table CXVI

1.0 Wt. normal solution. Expt. 2 at 60°. Cell L_5. Resistance, 30,000 ohms. Manometer 5. Calc. gas pressure, 27.167 atms. Time of setting up cell, March 25, 1911. Barometer during final record: max., 1.012; min., 0.976. Total daily pressures:

Final Record

	Atms.		Atms.		Atms.
Mar. 29,	29.319	Apr. 2,	29.377	Apr. 6,	29.399
30,	29.353	3,	29.405	7,	29.399
31,	29.331	4,	29.383	8,	29.421
Apr. 1,	29.358	5,	29.377		(11 days)

Mean total pressure, Mar. 29–Apr. 8 = 29.375 atms.
Mean barom. pressure, Mar. 29–Apr. 8 = 0.999 atm.
Mean osmot. pressure, Mar. 29–Apr. 8 = 28.376 atms.
Mean osmotic pressure for Expts. 1 and 2 = 28.3665 atms.
Ratio of osmotic to gas pressure = 1.044

Table CXVII

1.0 Wt. normal solution. Expt. 1 at 70°. Cell G_5. Resistance, 30,000 ohms. Manometer 28. Calc. gas pressure, 27.984 atms. Time of setting up cell, April 15, 1912. Barometer during final record: max., 1.016; min., 0.983. Total daily pressures:

Final Record

	Atms.		Atms.		Atms.
Apr. 19,	29.542	Apr. 22,	29.630	Apr. 25,	29.589
20,	29.558	23,	29.591	26,	29.607
21,	29.599	24,	29.585	27,	29.610

Mean total pressure, Apr. 19–27 = 29.590 atms.
Mean barom. pressure, Apr. 19–27 = 1.000 atm.
Mean osmot. pressure, Apr. 19–27 = 28.590 atms.

Table CXVIII

1.0 Wt. normal solution. Expt. 2 at 70°. Cell L_5. Resistance, 33,000 ohms. Manometer 5. Calc. gas pressure, 27.984 atms. Time of setting up cell, April 15, 1912. Barometer during final record: max., 1.016; min., 0.983. Total daily pressures:

Final Record

	Atms.		Atms.		Atms.
Apr. 17,	29.676	Apr. 21,	29.720	Apr. 25,	29.617
18,	29.623	22,	29.715	26,	29.646
19,	29.720	23,	29.635	27,	29.629
20,	29.746	24,	29.618		(11 days)

Mean total pressure, April 17–27 = 29.668 atms.
Mean barom. pressure, April 17–27 = 0.997 atm.
Mean osmot. pressure, April 17–27 = 28.671 atms.

Table CXIX

1.0 Wt. normal solution. Expt. 3 at 70°. Cell E_5. Resistance, 20,000 ohms. Manometer 1. Calc. gas pressure, 27.984 atms. Time of setting up cell, April 15, 1912. Barometer during final record: max., 1.016; min., 0.983. Total daily pressures:

Final Record

	Atms.		Atms.		Atms.
Apr. 18,	29.572	Apr. 22,	29.617	Apr. 25,	29.587
19,	29.602	23,	29.610	26,	29.646
20,	29.602	24,	29.590	27,	29.632
21,	29.602				(10 days)

Mean total pressure, April 18–27 = 29.606 atms.
Mean barom. pressure, April 18–27 = 0.999 atms.
Mean osmot. pressure, April 18–27 = 28.607 atms.

Table CXX

1.0 Wt. normal solution. Expt. 4 at 70°. Cell R_5. Resistance, 33,000 ohms. Manometer 15. Calc. gas pressure, 27.984 atms. Time of setting up cell, April 15, 1912. Barometer during final record: max., 1.016; min., 0.983. Total daily pressures:

Final Record

	Atms.		Atms.		Atms.
Apr. 18,	29.608	Apr. 22,	29.628	Apr. 25,	2.9596
19,	29.628	23,	29.600	26,	29.647
20,	29.635	24,	29.590	27,	29.700
21,	29.621				(10 days)

Mean total pressure, April 18–27 = 29.625 atms.
Mean barom. pressure, April 18–27 = 0.999 atm.
Mean osmot. pressure, April 18–27 = 28.626 atms.
Mean osmotic pressure for Expts. 1, 2, 3 and 4 = 28.6235 atms.
Ratio of osmotic to gas pressure = 1.0228

Table CXXI

1.0 Wt. normal solution. Expt. 1 at 80°. Cell H_5. Resistance, 10,500 ohms. Manometer 31. Calc. gas pressure, 28.801 atms. Time of setting up cell, May 27, 1912. Barometer during final record: max., 1.000; min., 0.986. Total daily pressures:

Final Record

	Atms.		Atms.		Atms.
May 28,	29.838	May 30,	29.801	May 31,	29.780
29,	29.811				

Mean total pressure, May 27–31 = 29.808 atms.
Mean barom. pressure, May 27–31 = 0.992 atm.
Mean osmot. pressure, May 27–31 = 28.816 atms.

Table CXXII

1.0 Wt. normal solution. Expt. 2 at 80°. Cell L_5. Resistance, 10,000 ohms. Manometer 1. Calc. gas pressure, 28.801 atms. Time of setting up cell, May 27, 1912. Barometer during final record: max., 1.002; min., 0.993. Total daily pressures:

Final Record

	Atms.		Atms.		Atms.
May 31,	29.770	June 3,	29.799	June 6,	29.859
June 1,	29.863	4,	29.785	7,	29.799
2,	29.836	5,	29.829		

Mean total pressure, May 31–June 7 = 29.8175 atms.
Mean barom. pressure, May 31–June 7 = 0.998 atm.
Mean osmot. pressure, May 31–June 7 = 28.8195 atms.
Mean osmotic pressure for Expts. 1 and 2 = 28.8178 atms.
Ratio of osmotic to gas pressure = 1.000

Table CXXIII

0.1 Wt. Normal Sol.

30°

	Atms.
No. 1,	2.4756
2,	2.4721
3,	2.4682
4,	2.4796
Mean,	2.474
Ratio,	1.000

40°

	Atms.
No. 1,	2.5546
2,	2.5616
3,	2.5630
Mean,	2.5597
Ratio,	1.003

50°

	Atms.
No. 1,	2.643
2,	2.6338
3,	2.629
Mean,	2.6353
Ratio,	1.000

60°

	Atms.
No. 1,	2.7202
2,	2.7142
Mean,	2.7172
Ratio,	1.000

0.2 Wt. Normal Sol.

30°

	Atms.
No. 1,	5.0397
2,	5.0478
Mean,	5.0438
Ratio,	1.020

40°

	Atms.
No. 1,	5.168
2,	5.158
Mean,	5.163
Ratio,	1.011

50°

	Atms.
No. 1,	5.2733
2,	5.2850
3,	5.2770
Mean,	5.2784
Ratio,	1.0016

60°

	Atms.
No. 1,	5.450
2,	5.4246
Mean,	5.4373
Ratio,	1.0008

0.3 Wt. Normal Sol.

30°

	Atms.
No. 1,	7.6409
2,	7.6526
Mean,	7.6468
Ratio,	1.031

Table CXXIII—(Continued)

40°

	Atms.
No. 1,	7.817
2,	7.853
3,	7.831
4,	7.835
Mean,	7.844
Ratio,	1.024

50°

	Atms.
No. 1,	7.960
2,	7.9879
3,	7.9737
Mean,	7.9739
Ratio,	1.0087

60°

	Atms.
No. 1,	8.1522
2,	8.1283
Mean,	8.1403
Ratio,	0.999

0.4 Wt. Normal Sol.

30°

	Atms.
No. 1,	10.305
2,	10.285
Mean,	10.295
Ratio,	1.040

40°

	Atms.
No. 1,	10.599
2,	10.6025
3,	10.6067
4,	10.5864
Mean,	10.5987
Ratio,	1.0377

50°

	Atms.
No. 1,	10.737
2,	10.710
Mean,	10.724
Ratio,	1.017

60°

	Atms.
No. 1,	10.871
2,	10.853
3,	10.873
Mean,	10.866
Ratio,	1.000

0.5 Wt. Normal Sol.

30°

	Atms.
No. 1,	12.9804
2,	12.9754
Mean,	12.9779
Ratio,	1.050

40°

	Atms.
No. 1,	13.349
2,	13.361
Mean,	13.355
Ratio,	1.046

50°

	Atms.
No. 1,	13.5148
2,	13.4927
3,	13.5037
Mean,	13.5037
Ratio,	1.025

60°

	Atms.
No. 1,	13.645
2,	13.6873
Mean,	13.6662
Ratio,	1.006

70°

	Atms.
No. 1,	13.991
2,	13.990
Mean,	13.9905
Ratio,	1.000

0.6 Wt. Normal Sol.

30°

	Atms.
No. 1,	15.706
2,	15.6937
3,	15.763
4,	15.690
Mean,	15.7132
Ratio,	1.0595

40°

	Atms.
No. 1,	16.137
2,	16.154
Mean,	16.146
Ratio,	1.054

50°

	Atms.
No. 1,	16.322
2,	16.306
Mean,	16.319
Ratio,	1.032

Table CXXIII—(Continued)

60°

	Atms.
No. 1,	16.519
2,	16.551
Mean,	16.535
Ratio,	1.014

70°

	Atms.
No. 1,	16.815
2,	16.824
Mean,	16.8195
Ratio,	1.0018

0.7 Wt. Normal Sol.

30°

	Atms.
No. 1,	18.4937
2,	18.5046
Mean,	18.4992
Ratio,	1.069

40°

	Atms.
No. 1,	18.962
2,	18.901
Mean,	18.932
Ratio,	1.0592

50°

	Atms.
No. 1,	19.2245
2,	19.1794
Mean,	19.2019
Ratio,	1.041

60°

	Atms.
No. 1,	19.4028
2,	19.4046
Mean,	19.4037
Ratio,	1.020

70°

	Atms.
No. 1,	19.553
2,	19.583
Mean,	19.568
Ratio,	0.999

0.8 Wt. Normal Sol.

30°

	Atms.
No. 1,	21.396
2,	21.354
Mean,	21.375
Ratio,	1.081

40°

	Atms.
No. 1,	21.779
2,	21.813
3,	21.819
4,	21.811
Mean,	21.8028
Ratio,	1.0674

50°

	Atms.
No. 1,	22.1285
2,	22.1035
Mean,	22.116
Ratio,	1.049

60°

	Atms.
No. 1,	22.344
2,	22.310
Mean,	22.327
Ratio,	1.027

70°

	Atms.
No. 1,	22.567
2,	22.567
Mean,	22.567
Ratio,	1.008

80°

	Atms,
No. 1,	23.062
Ratio,	1.001

0.9 Wt. Normal Sol.

30°

	Atms.
No. 1,	24.2146
2,	24.238
Mean,	24.2263
Ratio,	1.089

40°

	Atms.
No. 1,	24.738
2,	24.730
3,	24.738
Mean,	24.735
Ratio,	1.076

50°

	Atms.
No. 1,	25.132
2,	25.1136
Mean,	25.1228
Ratio,	1.0593

Table CXXIII—(Continued)

60°

	Atms.
No. 1,	25.2564
2,	25.275
Mean,	25.2657
Ratio,	1.0334

70°

	Atms.
No. 1,	25.559
2,	25.574
3,	25.554
Mean,	25.562
Ratio,	1.015

80°

	Atms.
No. 1,	25.915
2,	25.922
Mean,	25.919
Ratio,	1.000

1.0 Wt. Normal Sol.

30°

	Atms.
No. 1,	27.240
2,	27.2154
3,	27.242
4,	27.196
Mean,	27.2234
Ratio,	1.101

40°

	Atms.
No. 1,	27.673
2,	27.743
3,	27.688
Mean,	27.701
Ratio,	1.085

50°

	Atms.
No. 1,	28.199
2,	28.231
3,	28.196
Mean,	28.213
Ratio,	1.071

60°

	Atms.
No. 1,	28.357
2,	28.376
Mean,	28.3665
Ratio,	1.044

70°

	Atms.
No. 1,	28.590
2,	28.671
3,	28.607
4,	28.626
Mean,	28.6235
Ratio,	1.0228

80°

	Atms.
No. 1,	28.816
2,	28.8195
Mean,	28.8178
Ratio,	1.000

Table CXXIV

Weight-normal concentration

Mean osmotic pressure in atmospheres

Temp.	0.1	0.2	0.3	0.4	0.5	0.6	0.7	0.8	0.9	1.0
0°	(2.462)	4.722	7.085	9.442	11.895	14.381	16.886	19.476	22.118	24.825
5°	2.452	4.818	7.198	9.608	12.100	14.605	17.206	19.822	22.478	25.283
10°	2.498	4.893	7.334	9.790	12.297	14.855	17.503	20.161	22.884	25.693
15°	2.541	4.985	7.476	9.949	12.549	15.144	17.815	20.535	23.305	26.189
20°	2.590	5.064	7.605	10.137	12.748	15.388	18.128	20.905	23.717	26.638
25°	2.634	5.148	7.729	10.296	12.943	15.624	18.434	21.252	24.126	27.053
30°	2.474	5.044	7.647	10.295	12.978	15.713	18.499	21.375	24.226	27.223
40°	2.560	5.163	7.844	10.599	13.355	16.146	18.932	21.803	24.735	27.701
50°	2.635	5.278	7.974	10.724	13.504	16.319	19.202	22.116	25.123	28.213
60°	2.717	5.437	8.140	10.866	13.666	16.535	19.404	22.327	25.266	28.367
70°	...	...	...	....	13.991	16.820	19.568	22.567	25.562	28.624
80°	...	...	...	....	....	....	....	23.062	25.919	28.000
90°	...	...	...	....	....	....	....	....	....	....
100°	...	...	...	....	....	....	....	....	....	....

Table CXXV

Temp.	Weight-normal concentration									
	0.1	0.2	0.3	0.4	0.5	0.6	0.7	0.8	0.9	1.0
	Ratio of osmotic to gas pressure									
0°	(1.106)	1.061	1.061	1.060	1.069	1.077	1.083	1.093	1.104	1.115
5°	1.082	1.063	1.058	1.059	1.067	1.074	1.084	1.093	1.102	1.115
10°	1.082	1.060	1.059	1.060	1.066	1.073	1.083	1.092	1.102	1.113
15°	1.082	1.061	1.061	1.059	1.068	1.073	1.083	1.093	1.102	1.115
20°	1.084	1.062	1.060	1.060	1.067	1.073	1.084	1.093	1.103	1.115
25°	1.084	1.059	1.060	1.059	1.065	1.071	1.083	1.093	1.102	1.113
	(1.083)	(1.061)	(1.060)	(1.060)	(1.067)	(1.074)	(1.083)	(1.093)	(1.103)	(1.114)
30°	1.000	1.020	1.031	1.040	1.050	1.060	1.069	1.081	1.089	1.101
40°	1.003	1.011	1.024	1.038	1.046	1.054	1.059	1.067	1.076	1.085
50°	1.000	1.002	1.009	1.017	1.025	1.032	1.041	1.049	1.059	1.071
60°	1.000	1.001	0.999	1.000	1.006	1.015	1.020	1.027	1.033	1.044
70°	...	...	...	...	1.000	1.002	0.999	1.008	1.015	1.023
80°	...	...	...	...	...	...	...	1.001	1.000	1.000
90°	...	...	...	...	...	...	...	...	...	...
100°	...	...	...	...	...	...	...	...	...	...

Tables II to CXXII, inclusive, give somewhat detailed records of the individual experiments.

Table CXXIII contains, for each concentration of solution and each temperature, the observed osmotic pressures, their mean values, and the ratios of osmotic to calculated gas pressures. It is recalled in this connection—for the information of those who are not familiar with the earlier papers—that the standard for the calculation of the gas pressure of the solute is *not* the volume of the solution, *but the volume of the solvent in pure condition and at the temperature of maximum density, i. e., at 4° C.* It is to be noted, also, that the value 0.00367*t* has been employed in all calculations of pressure; hence, in so far as this coefficient is incorrect for nitrogen gas at the higher pressures, a correction is still to be applied to the osmotic pressures which are recorded in the tables.

Table CXXIV gives, for each of the 10 concentrations of solution, the osmotic pressures which have been found between 0° and the highest temperature at which we have worked up to the present time. This "highest temperature" was 60° for the 0.1, 0.2, 0.3 and 0.4 weight-normal solutions; 70° for the 0.5, 0.6 and 0.7 weight-normal concentrations; and 80° for the 0.8, 0.9 and 1.0 normal solutions. The work between 0° and 25° was reported in our last paper,[1] but is included in order that the pressures at the lower temperatures may be readily compared with those which were observed at the higher temperatures.

In Tables CXXV the osmotic pressure given in Table CXXIII are stated in the more convenient form of ratios of osmotic to gas pressure.

The obvious conclusions to be drawn from Table CXXV are:

1. Between 0° and 25°, all concentrations of cane sugar solutions, from 0.1 to 1.0 weight-normal, obey strictly the law of Gay-Lussac for gases. The same is true of the 0.1 normal solution between 30° and 60°, and of the 0.2 normal solution between 50° and 60°. In all of the cases cited the

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[1] This Journal, 45, 554.

ratio of osmotic to gas pressure is constant within the specified ranges of temperature.

2. Between 25° and 30°, the ratio of osmotic to gas pressure (which is constant, but greater than unity from 0° to 25°) begins to decline in all concentrations, but relatively more rapidly in the more dilute solutions.

3. The decline in ratio, which begins between 25° and 30°, continues at the higher temperatures until osmotic pressure becomes, in every instance, equal to the calculated gas pressure of the solute. It is not yet obvious whether the unit ratio, once reached, will be maintained at all higher temperatures; but the conduct of the 0.1 normal solution between 30° and 60°, and of the 0.2 normal solution between 50° and 60°, throws some light upon this important question.

4. The law of Boyle will be found to hold in four cases in Table CXXV; namely: (1) in that of the 0.1 and 0.2 normal solutions at 50°; (2) in that of the 0.1, 0.2, 0.3 and 0.4 normal solutions at 60°; (3) in that of the 0.5, 0.6, and 0.7 normal solutions at 70°; and (4) in the case of the 0.8, 0.9 and 1.0 normal solutions at 80°. On the other hand, there is nowhere to be found in the table any convincing evidence that the law of Boyle does not hold for osmotic pressure.

The blank spaces in Tables CXXIV and CXXV indicate the field which we hope to investigate during the coming year, but it is by no means certain that we shall be able to carry on the work at temperatures much above 80°. At this temperature, and even at 70°, the accurate measurement of osmotic pressure is costly and enormously difficult. The following statement will serve to illustrate its costliness. The measurement of osmotic pressure at 30° was begun with an equipment of 16 manometers, the preparation of which has cost us more than a year's labor—the average time required for the complete investigation of a manometer being about one month. During the course of the work between 60° and 80°, 12 of these instruments were put out of commisssion, half of them permanently.

Johns Hopkins University,
June, 1912

REVIEWS

COCOA AND CHOCOLATE, THEIR CHEMISTRY AND MANUFACTURE. By R. WHYMPER. Philadelphia: P. Blakiston's Son & Co. 1912. pp. xi + 327. Price, $5.00.

In this exhaustive English work the author states that "for the first time the chemical composition of cocoa has been traced from the fresh beans through the various stages of manufacture, so that the changes which occur during fermentation, drying, roasting, etc., may be followed." The subject is divided into three parts, dealing respectively with the history, botany, and agriculture of cocoa; manufacture of chocolates and cocoa powders; chemistry of cocoa. The history and growth of the cocoa industry is written in a very interesting and informing manner, being traced from the days of Cortes. Some startling figures are presented to show the phenomenal growth of this industry. For the decade ending 1908, the consumption of coffee in the United Kingdom remained practically stationary, while that of cocoa increased from 39,000,000 to 57,000,000 pounds per annum. For the year ending June 30, 1909, the United States was at the head of all cocoa-consuming countries, 130,000,000 pounds of cocoa being used during that period. A brief chapter is given to the botany and nomenclature of the different varieties of cocoa. Discussing the agriculture of cocoa, the author treats of such important features as selection of site, soil, manure and seed, and describes the best methods of planting and of combating various diseases, together with observations upon pruning and picking. Information on this subject appears to be comprehensive and practical and should be of great value to those intending to engage in the culture of cocoa. The great importance of properly fermenting the beans is emphasized and tables of analyses are given to show what changes occur in cocoa beans during this process. Washing, drying and polishing follow the fermentation.

The characteristics of the principal kinds of commercial cocoa beans are then discussed, together with the output of each. The author then deals with the composition of raw cocoa beans, giving tables of analyses from well known workers in this field. Various details of the manufacture of chocolates and cocoa powders are faithfully presented, illustrated by photographs of the modern machinery now in use. Analyses of the bean before and after roasting are given to show what changes take place during this process, and subsequent tables to illustrate losses and changes sustained by the beans at other stages of their passage through the factory. So-called soluble cocoa powders are discussed and the different methods of the application of alkali in preparing these are presented in detail. This is followed by analyses of various commercial cocoa powders and a discussion of interpretation of results of analysis of these products. The preparation of chocolate and various chocolate products, together with analyses of the same, is taken up in a thorough manner and many receipts for making these preparations are given. This part of the book dealing with the various manufacturing processes now in use is exhaustive and modern in its treatment of this phase of the subject. Part III, which concerns itself with the chemistry of cocoa, begins with a survey of the component parts of roasted cocoa beans, dealing first with the husk and then with the nibs. The different constituents of both are treated in a scientific way and many tables of analyses are given to support the text. In a similar manner the component parts of cocoa powders, chocolate and milk chocolates are treated. A short chapter on microscopical examination of cocoa preparations describes the normal appearance of cocoa under the microscope, and discusses the various adulterants which may be expected. In the chapters on methods of analysis, the author discusses the most recent methods and recommends only those which he himself has found to give accurate results. This resolution seems to have been followed and the methods appearing are mostly those which deserve a place in such a book.

The author is not quite correct, however, in stating that a modification of the Kunze and Decker method for xanthine bases, and the Dubois method for the determination of lactose and sucrose in milk chocolate, are recommended by the A. O. A. C. These methods have only been adopted as provisional by the association and subsequent work proved the latter less reliable than at first supposed, so that it has not been adopted as an official method. The form in which the method is now before the association for consideration prior to official adoption is materially different from that which was originally presented, in that the polarization at 87° for the determination of lactose is discontinued, calculation of this constituent being made entirely from the same polarizations as are used in the sucrose calculation.

Following the chapters on methods are the provisional definitions and standards of cocoa preparations adopted at the Congress of Cocoa and Chocolate Makers, held at Byrne in August, 1911, and a bibliography of some of the more important literature on the subject. The book as a whole is excellent and is a valuable addition to the literature upon the

subject and should prove of great assistance to those working in this field.
W. L. DUBOIS

DIE ELEKTROCHEMISCHEN VERFAHREN DER CHEMISCHEN GROSS-INDUSTRIE, ihre Prinzipien und ihre Ausführung. Von DR. JEAN BILLITER, Privatdozent an der Universität Wien. II Band: Elektrolysen mit unlöslichen Anoden ohne Metallabscheidung. Mit 228 Figuren und 53 Tabellen im Text und einem Anhang: Neuerungen der letzten Zeit auf dem Gesamtgebiete der technischen Elektrolyse wässriger Lösungen. Mit 9 Figuren im Text. Halle a. S.: Verlag von Wilhelm Knapp. 1911. pp. ix + 535. Price, M. 28.50.

The author contemplates writing a treatise of four volumes which is to cover the whole field of electrochemical endeavor. In 1909 he brought out Vol. I,[1] which dealt with the electrodeposition of metals from aqueous solutions, using principally soluble anodes. The present volume discusses electrolytic processes in which no metal is plated out, and the anodes used are mainly insoluble. The remaining two volumes are to treat of pyroelectrolytic and electrothermic processes. The subject of the volume under consideration is taken up under the three main heads, electrolysis of water, of chloride solutions, and of bromide solutions. There is added an appendix in which are brought together the improvements in the electrodeposition of metals which have been published since 1909, as well as those relating to the subject of Vol. II which have become known since the manuscript went to press. The whole subject is thus brought to date of publication.

The author has discussed principles and practice. Principles are common property, practice is not. In treating the latter a writer is at a great disadvantage in that most of the electrolytic plants do not allow descriptions of apparatus to be published nor any information to be given out. Most of the illustrations in the book therefore have to be diagrammatic sketches, reproductions of patent specifications, or some other form of general illustration, which explains the principles, but omits the important details. This discussion of practice is unfortunate, but cannot be helped under the prevailing policy of secrecy which seems to be increasing in electrolytic lines. The author has done as well as could be expected, he has given clear expositions of principles, and illustrated the practice in a general way as far as information was available. The reader who knows the full details of one process or another will find the descriptions inadequate, but he will profit by the general discussion of this process which may furnish a better general view than the specialist possesses. The book is a welcome addition to the technical literature.
H. O. HOFMAN

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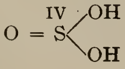
[1] THIS JOURNAL, **43**, 472.

Das Hydrosulfit. Teil I. Grundzüge der physikalischen Chemie des Hydrosulfits im Vergleich zu analogen Schwefelsauerstoffderivaten. Von Dr. Karl Jellinek, Ph.D., Privatdozent an der Technischen Hochschule zu Danzig. Mit 15 Kurven. Sammlung chemischer und chemisch-technischer Vorträge, begründet von F. B. Ahrens, herausgegeben von Prof. Dr. W. Herz, Breslau. XVII Band. 1–5 Heft. Stuttgart: Verlag von Ferdinand Enke. 1911. Price, M. 6.

This is the first book which has been written to illustrate the application of the principles of theoretical chemistry in the case of a typical reducing agent, hydrosulphite. It should prove as valuable to advanced students of chemistry as Abel's well known book on a typical oxidizing agent, hypochlorite.

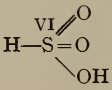
The principal topics discussed are as follows: Methods of analysis; the ordinary preparation of pure, stable, anhydrous hydrosulphite; the molecular formula; the constitution in comparison with that of other sulphur-oxygen compounds; aldehyde compounds of hydrosulphite; the constitutional formula; the heterogeneous equilibria in the binary system, $H_2O{-}Na_2S_2O_4$, including the determination of the transition point, $Na_2S_2O_4{-}Na_2S_2O_4 . 2H_2O$; conductivity and ionization of the oxygen acids of sulphur, and of the sodium salts; calculation of the ionization constants of the acids from the conductivity data for these acids and for the acid salts, and from electromotive force measurements with a hydrogen electrode; electromotive force corresponding to the reaction $S_2O_4^{--} + 2H_2O = 2HSO_3^- + H_2$; the electrolytic preparation of hydrosulphite from sulphate. A second monograph is promised which will deal more in detail with the inorganic, organic and technical chemistry of hydrosulphite.

Much of the material here presented is based on the recent experimental work of a single investigator, the author, and some of the results may therefore be altered by future investigators. Furthermore, owing to the variety of theoretical subjects discussed, it is obvious that any chemist will be able to find specific instances in which he disagrees with the author's conclusions, or in which he would like to alter the method of presentation. The reviewer, for example, considers that the chapter on the constitution of sulphur-oxygen compounds would be much improved by the introduction of the idea of positive and negative valences already adopted by so many chemists. The author has assigned to sulphur in the symmetric and asymmetric forms of sulphurous acid the valences four and six,



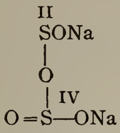
$O = \overset{IV}{S}\langle{}^{OH}_{OH}$

and



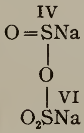
$H{-}\overset{VI\,\nearrow O}{S}{=}O \;\; {}_{\searrow OH}$

but would it not be much simpler to consider that in each case the valence of sulphur is +4? The latter method has the advantage that each process of oxidation corresponds to a definite increase of the positive valence or to a definite decrease of the negative valence of some element, and that the equation for any oxidation-reduction reaction may be written at once when the initial and final substances are known. The average valence of sulphur in sodium hydrosulphite is +3, but the author presents evidence to show that the formula is either



$$\begin{array}{l}\quad\ \overset{\mathrm{II}}{\mathrm{SONa}}\\ \quad\ \ |\\ \quad\ \ \mathrm{O}\\ \quad\ \ |\ \mathrm{IV}\\ \mathrm{O{=}S{-}ONa}\end{array}$$

or



$$\begin{array}{l}\overset{\mathrm{IV}}{\mathrm{O{=}SNa}}\\ \quad\ \ |\\ \quad\ \ \mathrm{O}\\ \quad\ \ |\ \mathrm{VI}\\ \quad \mathrm{O_2SNa}\end{array}$$

from which it is evident that the valences of the sulphur atoms are +2 and +4, respectively. WILLIAM C. BRAY

STAND UND WEGE DER ANALYTISCHEN CHEMIE. Von PROF. DR. WILHELM BÖTTGER, Universität Leipzig. Die chemische Analyse: Sammlung von Einzeldarstellungen auf dem Gebiete der chemischen, technisch-chemischen und physikalisch-chemischen Analyse, herausgegeben von DR. B. M. MARGOSCHES, Privatdozent an der Deutschen Technischen Hochschule Brünn. XIII Band. Stuttgart: Verlag von Ferdinand Enke. 1911. pp. 55. Price, M. 1.80.

This interesting brochure deals with the present status of analytical chemistry as an art and as a branch of chemical science in a spirit of intelligent criticism which is most helpful and enlightening. The author writes from the viewpoint of one well informed regarding the advances of the science in physico-chemical fields, as well as that of one who is himself skilled in the operations and versed in the processes of analytical chemistry. His acquaintance with conditions prevailing in this country, as a consequence of his residence here, lend added value to his comments, and his evident appreciation of the work of Dr. W. F. Hillebrand should enlist the sympathy of American readers.

Dr. Böttger deplores the present subordinate position of analytical chemistry and the general defectiveness of much of the published work of chemical analysts, and also their indisposition to avail themselves of the aids which are now available from other branches of chemical science. This he ascribes in part to the faulty instructional methods, to the discussion of which he devotes a chapter of his monograph. In separate chapters he points out how the processes of gravimetric and volumetric analysis may be made more exact, and may be scientifically investigated by taking advantages of facts and principles which are the products of modern chemical research. As an appendix he gives a translation of Dr. Hillebrand's address entitled "Some Thoughts on the Present Condition of Analytical Chemistry," delivered in 1905, which is hardly less applicable to-day than at the time of its delivery.

A perusal of this pamphlet is to be heartily commended to teachers, investigators, and especially to practitioners.

H. P. TALBOT

A HANDBOOK OF ORGANIC ANALYSIS, QUALITATIVE AND QUANTITATIVE. By HANS THATCHER CLARKE, B.Sc. (Lond.), A.I.C., Lecturer on Stereochemistry in University College, London. With an Introduction by J. NORMAN COLLIE, PH.D., LL.D., F.R.S., Professor of Organic Chemistry in University College, London. New York: Longmans, Green & Co. pp. viii + 264. Price, $1.40.

In the introduction to this book Professor Collie shows the need that exists for it in the following words: "Organic analysis, qualitative and quantitative, has of recent years acquired increasing importance in the training of the chemist. And this with reason, for the examination of unknown organic compounds has, perhaps, an even greater educational value than has that of inorganic substances.

"At the present time hardly any books exist which deal with the systematic testing of organic substances. There are many that describe the preparation of organic substances, give quantitative methods, and deal with special analysis of distinct classes of compounds. But the book that would enable the chemist to find out qualitatively the nature of the multitudinous carbon derivatives met with in ordinary work in an organic laboratory—that book is wanted.

"It is by no means easy to arrange a general plan for testing organic compounds so that one can say for certain what the particular compound may be. But as organic chemistry is an eminently practical science, there ought to be good practical books dealing with the subject—books where the descriptions are concise, where the treatment of the subject is systematic and not merely an enumeration of special tests for special compounds, and where the student has to use his head as well as the information supplied by the text-book. Mr. Clarke has in this book recognized these requirements."

Again Professor Collie says: "The most important novelty, however, in the book is to be found in the chapter 'Tables of Compounds.' In this chapter Mr. Clarke has collected together the data that are wanted by the ordinary student after he has determined as far as possible the nature of the organic compound he is analyzing, i. e., the nature of the radicles present, its melting and boiling point, and possibly its molecular weight. Under ordinary conditions, after these data have been obtained, a lengthy hunt through a dictionary or manual of organic chemistry must be made to try to find what particular substance agrees with the facts discovered. In the 'Table of Compounds' a complete list is given of all the more important compounds to be met with, together with their properties, and thus much valuable time is gained through the possibility of making a direct comparison of the properties under investigation."

The first chapter is devoted to the preliminary investigation. The "Examination for Radicles" and "Separation of Organic Compounds" are the headings for Chapters Two and Three. Chapter Four contains the classified tables of common organic compounds, while Chapters Five and Six are given up to quantitative determinations of the constituent elements and radicals. Chapter Seven deals with the determination of some physical properties, such as molecular weight, vapor density, optical rotation, etc. There is an index of substances and also a good general index.

Mr. Clarke's book covers a great deal of ground and gives all that the average student should need. It will be of great assistance to any one testing organic substances, and will help to put quantitative organic chemistry on as systematic a basis as qualitative inorganic chemistry has been for many years.

W. R. O.

THE CHEMISTRY OF THE RADIO ELEMENTS. By FREDERICK SODDY, F.R.S., Lecturer in Physical Chemistry and Radioactivity in the University of Glascow. Monographs on Inorganic and Physical Chemistry. Edited by ALEXANDER FINDLAY, D.Sc. London, New York, Bombay and Calcutta: Longmans, Green & Co. 1911. pp. 92. Price, $0.90.

It may be desirable to separate the chemistry of the radioactive elements from the physics of radioactivity. But when we consider how little we really know of the chemistry of these substances as such, this appears to the reviewer to be very doubtful. The fact is that we have thus far not been able to obtain enough of the more highly radioactive substances to study them profitably by chemical methods—physical methods, in general, requiring much less material than chemical.

The transformations of uranium, radium, thorium and actinium constitute the chief subjects treated in this little booklet.

H. C. J.

PHYSICO-CHEMICAL CALCULATIONS. By JOSEPH KNOX, D.Sc., Lecturer on Inorganic Chemistry, University of Aberdeen. London: Methuen & Co., Ltd. pp. viii + 188. Price, 2s. 6d.

This book is based on Abegg and Sackur's "Physikalisch-chemische Rechenaufgaben,"[1] but instead of simply giving a short summary of the laws and formulas used in the problems, as in the German book, the subject matter has been arranged in chapters dealing with the main subdivisions of physical chemistry and a short introduction appended to each chapter, treating of the theory involved in the problems. In this way, and by the addition of many new problems, the contents of Abegg and Sackur's book have been almost doubled. The book should serve excellently in showing the student how to apply practically the various principles and formulas which he learns in the theoretical study of physical chemistry.

C. A. R.

A TEXT-BOOK OF INORGANIC CHEMISTRY. By DR. A. F. HOLLEMAN, Professor Ordinarius in the University of Amsterdam. Issued in English in coöperation with HERMON CHARLES COOPER. Fourth English edition, completely revised. New York: John Wiley & Sons; London: Chapman & Hall, Limited. 1912. pp. viii + 505. Price, $2.50.

Prof. Cooper says in the Preface: "The present edition represents a thorough revision of the work of the Dutch author and the American collaborator. It profits by the author's experience with the frequent editions in other languages but is independent in composition.

"Very many of the descriptive portions have been rewritten, notably those on the sulphur oxides and acids, sodium hydroxide and carbonate, radioactive elements and platinum, as well as the sections on thermochemistry, colloids and the iron-carbon system, while the subjects of stability and the reality of molecules and atoms furnish new material."

This book is so well known that it is only necessary to call attention to the fact that a new edition has appeared.

C. A. R.

LES NOUVEAUTÉS CHIMIQUES POUR 1911. Nouveaux Appareils de Laboratoire, Méthodes Nouvelles de Recherches appliquées à la Science et à l'Industrie. Par CAMILLE POULENC, Docteur ès Sciences. Avec 178 figures intercalées dans le texte. Paris: Librairie J.-B. Baillière et Fils. 1911. pp. viii + 354. Price, Fr. 4.

The 1911 volume of this Annual contains the usual interesting collection of descriptions of new forms of apparatus designed for the use of physicists, chemists and bacteriologists. It is well worth while glancing through. C. A. R.

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[1] See THIS JOURNAL, **44**, 110.

Vol. XLVIII August, 1912 No. 2

AMERICAN CHEMICAL JOURNAL

[Contributions from the Sheffield Laboratory of Yale University]

CC.—HYDANTOINS

THE ACTION OF POTASSIUM THIOCYANATE ON ASPARAGINE[1]

By Treat B. Johnson and Herbert H. Guest

[FOURTEENTH PAPER]

It is well known that the amount of sulphur in many proteins is much greater than can be accounted for on the assumption that cystine and cysteine are the only sulphur combinations which are present in these natural substances. Regarding the nature of other sulphur linkings, we have practically no knowledge. Evidence is available,[2] however, which indicates that thioamide groupings functionate in the synthesis of sulphur proteins. In order, therefore, to obtain new data which we believed would contribute to our present knowledge of these substances, we took up the study of N-unsubstituted thiohydantoins. Several papers on these compounds have already been published[3] and the investigation is still in progress. In this paper we shall describe some new thiohydantoin derivatives of aspartic acid.

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[1] The work described in this paper formed part of a thesis presented by Mr. Herbert Hartley Guest to the Graduate School of Yale University for the degree of Doctor of Philosophy.

[2] Johnson: J. Biol. Chem., **9**, 439.

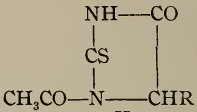
[3] J. Biol. Chem., **10**, 139; **11**, 97. J. Am. Chem. Soc., **33**, 1973. This Journal, **47**, 242.

The N-unsubstituted thiohydantoins have been made by the application of an entirely new reaction, viz., by the action of potassium thiocyanate on α-amino acids in the presence of acetic anhydride. The results which we have obtained apparently permit us to make the two following statements:

(1) Monobasic α-amino acids (I) combine with potassium thiocyanate in acetic anhydride solution, forming 3-acetylthiohydantoins (II) according to the following equation:

$$\underset{\text{I}}{R.CH(NH_2)COOH} + KSCN + (CH_3CO)_2O =$$

$$CH_3COOK + H_2O +$$



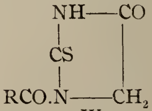
II

Every α-amino acid which we have so far examined has reacted in this manner.

(2) α-Acylamino acids (III) react with potassium thiocyanate in acetic anhydride solution, forming the corresponding 3-acylthiohydantoins (IV) as follows:

$$\underset{\text{III}}{RCONHCH_2COOH} + KSCN + (CH_3CO)_2O =$$

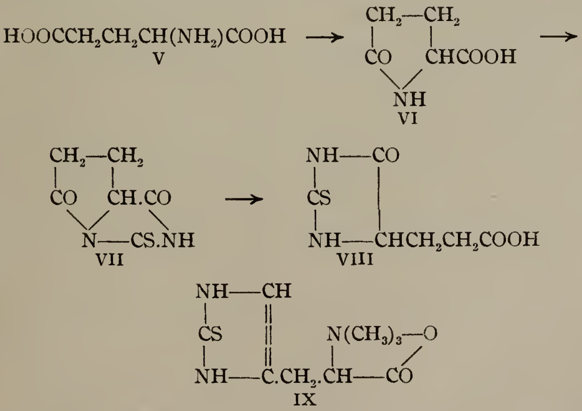
$$CH_3COOH + CH_3COOK +$$



IV

This reaction has been applied only with hippuric and aceturic acids and acetylalanine, but we propose, as soon as possible, to test its general application with other acyl derivatives. The unsubstituted thiohydantoins are formed quantitatively by the hydrolysis of their 3-acyl derivatives with hydrochloric acid. The sulphur atom is not removed by this treatment.

While the reaction (I) can be applied successfully with the monobasic amino acids, we were unable to obtain a thiohydantoin by the action of potassium thiocyanate on glutaminic acid.[1] This acid was deamidized under these conditions and in order to synthesize the hydantoin we started with pyrrolidonecarboxylic acid (VI) and applied Method (2). This acid combined smoothly with potassium thiocyanate, forming the bicyclic derivative (VII), which then underwent a normal hydrolysis with acids, giving the 2-thiohydantoin-4-propionic acid (VIII). The corresponding hydantoin derivative has been prepared by Dakin.[2] This thiohydantoin derivative (VIII) is of interest because of its relationship to *ergothioneine* (IX), which Tanret isolated from ergot of rye.[3] These various changes are represented by the following formulas:



V VI VII VIII IX

We have now made the interesting observation that aspartic acid (X) likewise reacts abnormally with potassium thiocyanate in acetic anhydride solution. It behaves in the same manner as glutaminic acid and is deamidized. In other words, the presence of the two carboxyl groups in these two acids apparently prevents the formation of thiohydantoins by the action of potassium thiocyanate. On the other hand, if the influence of one of the carboxyls is destroyed a thiohydantoin is formed almost quantitatively.

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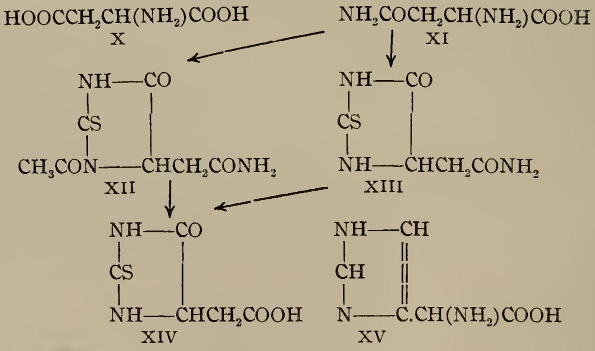
[1] Johnson and Guest: THIS JOURNAL, **47**, 242.

[2] *Ibid.*, **44**, 48.

[3] J. pharm. chim., **30**, 145. Compt. rend., **149**, 2222. Barger and Ewin: J. Chem. Soc., **1911**, 2336.

We now find that the thiohydantoin (XIV) can be obtained from asparagine (XI). This amide reacts normally with potassium thiocyanate according to Reaction (I), forming the acetylthiohydantoin (XII). The latter was then converted into the thiohydantoin of aspartic acid (XIV) by hydrolysis with hydrochloric acid. A secondary product of this reaction was 2-thiohydantoin-4-acetamide (XIII), which also gave on hydrolysis the thiohydantoin (XIV):



The structure of the thiohydantoin (XIV), and incidentally those of the hydantoins (XII) and (XIII), was established as follows: It was desulphurized when digested with chloroacetic acid, forming quantitatively the corresponding hydantoinacetic acid (XVI), whose constitution was definitely established by Gabriel.[1] This formation of a thiohydantoin derivative from asparagine is therefore a new proof that the $CONH_2$ group in this acid is joined to a different carbon than the amino radical. The isomeric derivative would be expected to combine with potassium thiocyanate and form a hexahydropyrimidine (XVII):

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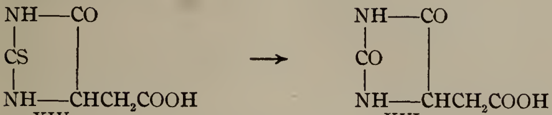
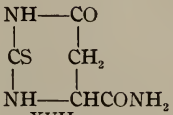
[1] Ann. Chem. (Liebig), **348**, 89.



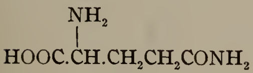
XIV XVI



XVII

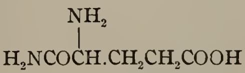
2-Thiohydantoin-4-acetic acid (XIV) is of particular interest because it has the same relation to aminoimidoazoleacetic acid (XV) as 2-thiohydantoin-4-propionic acid (VIII) has to histidine. Engeland[1] claims to have isolated this glyoxaline derivative (XV) from human urine in the form of its picrolonate, $C_5H_7O_2N_3 . C_{10}H_8O_5N_4$.

So far as the writer is aware, the constitution of glutamine has never been established. If this amide is to be assigned the structure (XVIII) corresponding to that of asparagine, then theoretically it should react with potassium thiocyanate with formation of a thiohydantoin derivative (XX). The writer hopes that some investigator, to whom this rare substance is available, will try this reaction and establish the constitution of this naturally occurring amino acid.



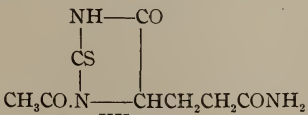
$HOOC.\overset{NH_2}{CH}.CH_2CH_2CONH_2$

XVIII



$H_2NCO\overset{NH_2}{CH}.CH_2CH_2COOH$

XIX



XX

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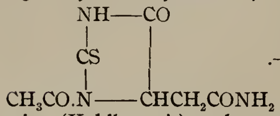
[1] Z. physiol. Chem., **57**, 49.

EXPERIMENTAL PART

The Action of Potassium Thiocyanate on Asparagine

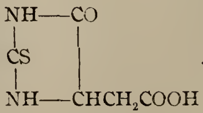


3-Acetyl-2-thiohydantoin-4-acetamide, .—Two grams of anhydrous asparagine (Kahlbaum's) and 1.5 grams of a carefully dried potassium thiocyanate were ground together to a fine powder and then suspended in 9 cc. of acetic anhydride to which 1 cc. of glacial acetic acid was added. The mixture was then heated on the water bath for 30 minutes. There was a slight effervescence and a clear, yellow solution was obtained. This was cooled and poured into 50 cc. of cold water, when this hydantoin separated in slender, prismatic crystals. The compound is readily soluble in hot but difficultly soluble in cold water and easily soluble in alcohol. It melts at 222°–223° with effervescence. The yield was 1.8 grams. Analysis (Kjeldahl):

	Calculated for $C_7H_9O_3N_3S$	Found
N	19.53	19.3

In another experiment, in which we used 10 grams of asparagine, the thiohydantoin separated from the acetic anhydride solution after cooling to 0°. In this manner we obtained 7.2 grams of the thiohydantoin. The acetic anhydride filtrate was then diluted with 200 cc. of water. No more thiohydantoin separated. The solution was then concentrated to a small volume at 100° and cooled, when *2-thiohydantoin-4-acetamide* separated. This was purified by recrystallization from hot water and melted at 246° with effervescence. Analysis (Kjeldahl):

	Calculated for $C_5H_7O_2N_3S$	Found
N	24.2	24.4



2-Thiohydantoin-4-acetic Acid, .—An excellent yield of this compound is obtained by hydrolysis of the above acetylthiohydantoin. Two grams of 3-acetyl-2-thiohydantoin-4-acetamide were digested for about one hour with hydrochloric acid. The acid solution was then concentrated to about one-half its original volume and cooled, when this thiohydantoin separated. It was purified for analysis by crystallization from hot water and deposited, on cooling, in hexagonal tables or plates, which melted at 222° with decomposition. The hydantoin is more soluble in alcohol than in water. A mixture of this compound with 3-acetyl-2-thiohydantoin-4-acetamide melted at 195°–198°.

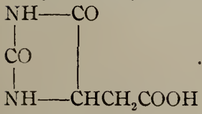
Carbon and nitrogen determinations:

I. 0.1145 gram substance gave 0.1430 gram CO_2 and 0.0400 gram H_2O.

Nitrogen determination (Kjeldahl):

	Calculated for $C_5H_6O_3N_2S$	Found	
		I	II
C	34.4	34.06	...
H	3.4	3.9	...
N	16.1	16.13	16.22

Hydantoin-4-acetic Acid (*Malyureidic Acid*),



.—This hydantoin was obtained by the desulphurization of 2-thiohydantoin-4-acetic acid. This was accomplished as follows: Two grams of 2-thiohydantoin-4-acetic acid were digested for 3 hours with 2 grams of chloroacetic acid dissolved in 10 cc. of water. The hydantoin dissolved on warming, giving an almost colorless solution. This was evaporated to dryness and the hydantoin purified by crystallization from boiling alcohol or water. It deposited, on cooling, in blocks. After repeated recrystallizations from alcohol the acid melted constant at 214°–215° in an open capillary tube. It did not give a test for sulphur. Analysis (Kjeldahl):

	Calculated for $C_5H_6O_4N_2$	Found
N	17.7	17.5

This same hydantoin has been obtained by Grimaux,[1] Guareschi,[2] Gabriel,[3] Lippich,[4] and Dakin.[5] These authors record various melting points from 207°–228°. These irregularities are probably due to mixtures of the active and racemic modifications. Dakin states that the pure inactive hydantoin melts at 225°–228°, first slightly sintering. It has been our experience that the decomposition point of this compound is indefinite and depends upon the mode of heating. An attempt to desulphurize 2-thiohydantoin-4-acetic acid by digestion with mercury oxide was not successful. For example, one gram of the thiohydantoin and an excess of moist mercury oxide were digested in water for about one hour. Mercury sulphide was formed and some mercury dissolved. After treatment with hydrogen sulphide to decompose any soluble mercury compounds and filtering, the solution was then evaporated to dryness. A semisolid residue was obtained, but no definite product was isolated. The hydantoin was apparently oxidized by the oxide.

The Action of Potassium Thiocyanate on Aspartic Acid

While aspargine reacts with potassium thiocyanate, aspartic acid does not combine smoothly with this reagent to form the corresponding hydantoin acid. The results obtained by us show that aspartic acid is deamidized by the action of potassium thiocyanate in acetic anhydride solution. We performed several experiments, using 2 grams of aspartic acid, 1.5 grams of the thiocyanate, 9 cc. of acetic anhydride and 1 cc. of acetic acid in each case. In only one experiment did we obtain any evidence of the formation of a 2-thiohydantoin derivative and then it was formed in so small an amount that it could not be purified. In order to explain this behavior we performed the following experiment:

The same proportions of acid, thiocyanate and anhydride were taken as described above and the mixture heated for 30

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[1] Ann. chim. phys., [5] **11**, 402 (1877). Compt. rend., **81**, 325. Bull. soc. chim., [2] **24**, 337.

[2] Beilstein's Handbuch, I, 1383.

[3] Ann. Chem. (Liebig), **348**, 87.

[4] Ber. d. chem. Ges., **41**, 2972, 2981.

[5] This Journal, **44**, 57.

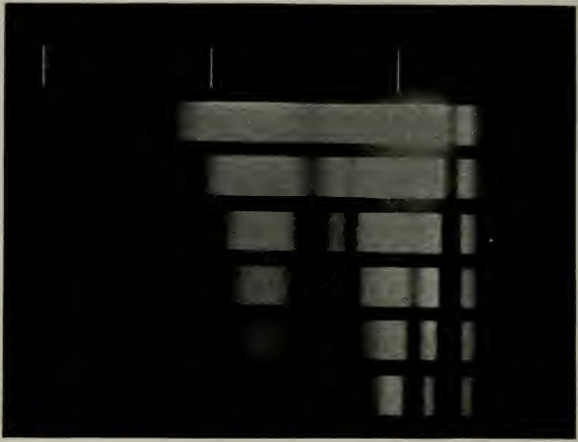

Plate I

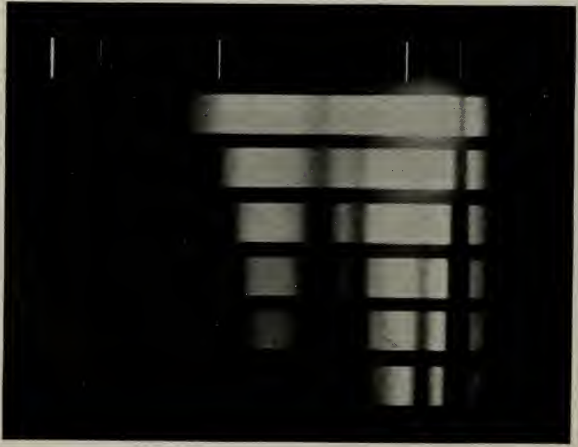

Plate II

minutes. There was a brisk evolution of gas and a clear yellow solution was obtained. This was cooled, diluted with an excess of dilute hydrochloric acid and the solution then evaporated to remove the excess of acid. A syrupy residue was obtained, which was transferred to a Kjeldahl flask, an excess of sodium hydroxide solution added, and the mixture then distilled. The distillate was collected in a beaker containing an excess of hydrochloric acid. After about 400 cc. had distilled over, the acid solution was then evaporated to dryness and the ammonium chloride dried and weighed. The results are given in the following table:

	Gram
NH_4Cl equivalent to N in aspartic acid	0.80
NH_4Cl equivalent to N in KSCN	0.80
Total NH_4Cl available	1.60
NH_4Cl obtained	1.30

In other words, over 80 per cent. of the nitrogen was recovered in the form of ammonium chloride. It is evident therefore, that the aspartic acid is deamidized and a thiohydantoin is not formed. 2-Thiohydantoin-4-acetic acid can be digested with dilute hydrochloric acid without decomposition.

New Haven, Conn.
May 27, 1912

METHODS FOR DETERMINING NEO- AND ALLOCHLOROPHYLL IN THE PRESENCE OF ONE ANOTHER

By C. A. Jacobson and L. Marchlewski

In our previous paper[1] we showed that the ratio of neochlorophyll to allochlorophyll in plants is not a constant one. This ratio is not only variable in different species of plants but may show variations in the same species, where the samples have been grown under different conditions.

Plant physiology and the study of the functions of chlorophyll have been greatly handicapped for the want of a sufficiently exact method for determining the ratio of the two components of this substance when present in small quantities of the green material.

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[1] This Journal, 47, 221.

Tswett[1] endeavored to work out a method which was based on the adsorptive properties of calcium carbonate for the two coloring matters. By this method he came to the conclusion that neo- and allochlorophyll are present in a constant proportion in all plants, which, in the light of more recent work, is manifestly erroneous.

In our work with various kinds of leaves we noticed the marked difference which the ultraviolet spectra presented. Nettle and *Acer negundo*, for example, were fundamentally different in this respect. A study of these varieties, together with the spectrum of allochlorophyllan, led us to surmise that the band characterized by wave lengths $\lambda = 436.5–442.8$ was entirely due to the latter substance, whereas the band in the region $\lambda = 391.8–399.7$ was produced by neochlorophyllan; but since we did not have this substance in a pure state, a positive statement could not be made. We noticed, further, that only minute quantities of material are necessary for producing these absorption bands so that we directed our efforts for obtaining the desired method along this line, but it is obvious that the success of our attempts would depend upon whether or not we could prepare neochlorophyllan in pure condition.

This we succeeded in doing by two entirely different methods. The one starting with chlorophyllan, the first acid derivative of chlorophyll, is the shorter and less cumbersome and will therefore be given precedence.

Method 1.—Two grams chlorophyllan, obtained as described in our previous paper, were dissolved in a liter of ether and shaken vigorously together with 200 cc. concentrated hydrochloric acid for a few minutes in a separatory funnel, during which time the funnel was cooled under the water tap. The liquids were allowed to separate, after which the acid portion was drawn off and shaken with two successive 250 cc. portions of ether. By this treatment the phylloxanthin was removed,

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[1] Ber. d. bot. Ges., **24**, 384 (1908).

Plate III

Plate IV

leaving the neochlorophyllan in the acid. The acid portion was then poured into 2 liters of water and extracted with one liter of ether. The ether solution thus obtained was shaken with 250 cc. of 10 per cent. hydrochloric acid and the liquids allowed to separate. The acid had only a slight color, but after the next extraction with 1 liter of 15 per cent. hydrochloric acid the latter was deeply colored dark blue by reflected and bluish purple by transmitted light. The 15 per cent. hydrochloric acid served to remove the phyllocyanin that was formed from the neochlorophyllan by the action of the concentrated acid. This treatment was repeated once or twice, after which the ethereal solution was extracted with an equal volume of 20 per cent. hydrochloric acid and this shaking repeated two or three times until the acid separated with only a slight yellowish green color. The ether was then freed entirely from acid by successive washings with water, after which the ether was distilled off and the resulting neochlorophyllan taken up in chloroform and precipitated with alcohol in the ordinary way. Neochlorophyllan is a black, amorphous substance, having an odor suggesting oak bark. In solution it has a deep olive-green color and is easily distinguishable from a solution of allochlorophyllan, which has a reddish brown color. In the following table will be found the measurements of the five absorption bands of neochlorophyllan in the visible part of the spectrum.

Plate I represents a photograph of the absorption bands of this substance in the visible spectrum, the solvent, concentration and thickness of layers being the same as those given in the above table. Five absorption bands are seen which are essentially the same as those described for nettle chlorophyllan, with the exception that the fourth band of the neochlorophyllan is narrower and better defined. In the 3- and 5-mm. layers we noticed light streaks in the centre of the first and fifth bands, and these can be seen in the negatives but are lost in the prints and reproductions. We also noticed a faint shading which was only a suggestion of a sixth band located between the blue and violet part of the spectrum. In ethereal solu-

Table I.—Spectrum of Neochlorophyllan

Concentration: 0.0004 gram per cc. chloroform

Thickness of layer	1.5 mm.	3 mm.	5 mm.	7 mm.
Band I	λ 676.5–660.2	λ 680.5–656.0	λ 685.2–654.0	λ 687.7–650.5
" II	λ 613.4–600.3	λ 615.0–600.7	λ 616.4–599.8	λ 617.7–599.4
" III	....	....	λ 567.7–558.2	λ 568.1–558.2
" IV	λ 541.2–532.7	λ 541.5–533.0	λ 543.1–532.7	λ 543.7–531.6
" V	λ 513.0–499.2	λ 513.8–497.7	λ 514.5–496.5	λ 514.7–496.2

Thickness of layer	9 mm.	11 mm.
Band I	λ 690.0–647.4	λ 692.0–621.8
" II	λ 620.8–598.6	λ 621.4–595.5
" III	λ 570.2–556.2	λ 571.2–555.6
" IV	λ 545.0–531.6	λ 545.7–529.8
" V	λ 515.9–494.4	λ 517.3–493.9

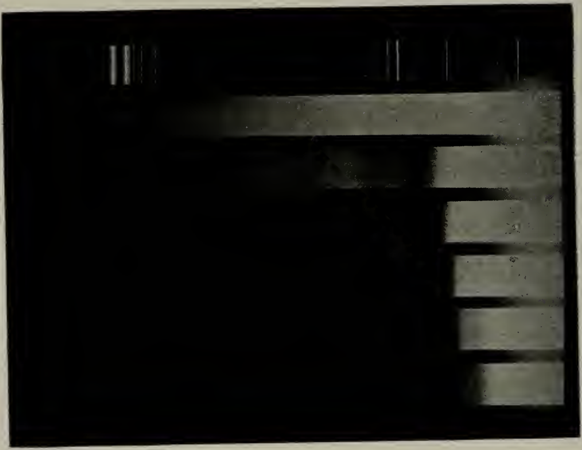

Plate V

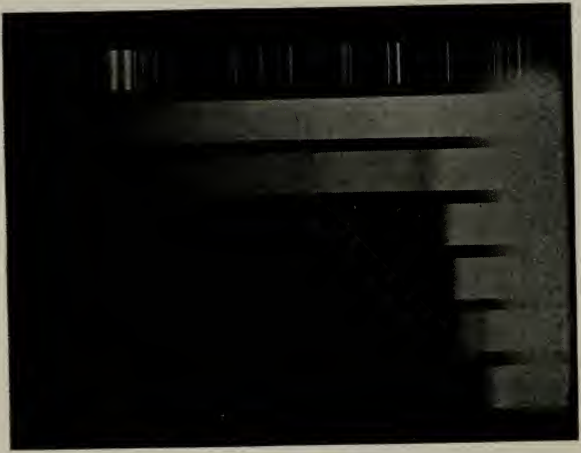

Plate VI

tions this band comes out stronger and could be measured with some degree of accuracy.

The ultraviolet spectrum of neochlorophyllan is, however, by far the more interesting and serves as the basis for the present method of determining the two coloring matters in the presence of one another. Plate IV represents the ultraviolet spectrum of neochlorophyllan obtained by the foregoing method. The plate shows only three absorption bands, which are recorded in wave lengths in the following table. The readings were taken from the negative in correlation to the lines of the copper spectrum, while the helium lines furnished the fixed points for the measurements in the visible portion.

Table II.—Neochlorophyllan Spectrum

Concentration: 0.00004 gram per cc. chloroform

Thickness of layer mm.	Band III	Band II	Band I
2	....	λ 394.0–403.0	λ 409.6–421.3
4	λ 366.4–381.3	λ 391.0–404.1	λ 408.4–424.0
6	λ 365.0–382.7	λ 388.8–405.0	λ 407.4–426.5
8	λ 364.0–383.8	λ 387.2	428.8
10	λ 361.5		430.5
12	λ 357.4		432.5

By comparing the above readings with those obtained for nettle, *Platanus occidentalis* or any other of the chlorophyllans measured and recorded in our previous paper, the neochlorophyllan bands may be easily located.

From the work of Marchlewski and Marszalek[1] we learn that the chlorophyllan obtained from the leaves of *Acer platanoides* (1910) had a phytol content of 34.24 per cent., whereas the allochlorophyllan separated from that mixture contained only 30.75 per cent. when the substance was dried in a vacuum desiccator or 32.85 per cent. after drying at 105°. The same experimenters also found that the methoxyl contained in the above-mentioned chlorophyllan amounted to 3.44 per cent., whereas the corresponding allochlorophyllan yielded only 3.15 per cent.; it was interesting to know what values would be obtained in the case of neochlorophyllan.

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[1] Biochem. Z., **35**, 413 (1911).

The following are the results obtained from this substance, isolated and purified by the method already described. The phytol was dried to constant weight in a vacuum desiccator over sulphuric acid:

1.6462 grams neochlorophyllan gave 0.5480 gram phytol, or 33.3 per cent.

0.3191 gram neochlorophyllan gave 0.0796 gram AgI, or 3.29 per cent. OCH_3.

We also wish to present the second method by which neochlorophyllan was obtained in pure condition, and this is especially significant for the reason that the product is extracted directly from the leaves by means of organic solvents alone. No acids or alkalis were used at any stage of the process, except at the end, when the pure neochlorophyll was converted into its acid derivative.

Making use of the results of Sorby[1] and Marchlewski and Schunck[2] for the preparation of pure chlorophyll we finally developed a method which led to the desired result.

Method 2.—Three liters of cold 92 per cent. alcohol were poured on 1 kilogram of dried and finely ground *Acer platanoides* leaves and the mixture allowed to stand for one hour, after which the alcoholic extract was pressed out under 300 atmospheres. The filtered extract showed an extinction coefficient for sodium light of 6.32. One liter of this extract was shaken with 100 cc. petroleum ether and allowed to stand. Twenty-five cc. of water were added to make the liquids separate more quickly. After letting off the alcoholic portion, this was shaken with 800 cc. carbon disulphide. The latter solvent was then separated, measuring 850 cc., which was in turn shaken with an equal volume of 82 per cent. alcohol. A few cc. of 95 per cent. alcohol were added to facilitate the separation. This shaking with 82 per cent. alcohol was carried out three successive times, after which 365 cc. carbon disulphide solution remained. The latter was then shaken with an equal volume of 85 per cent. alcohol. From this mixture 240 cc. carbon disulphide solution separated, which was

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[1] P. Roy. Soc., **21**, 442 (1873).

[2] J. Chem. Soc., **77**, 1080 (1900).

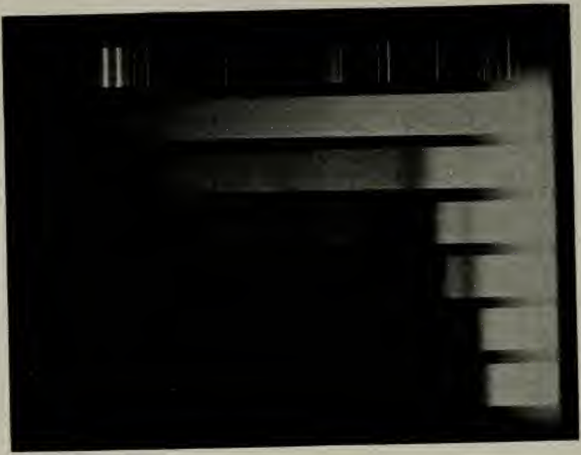

Plate VII

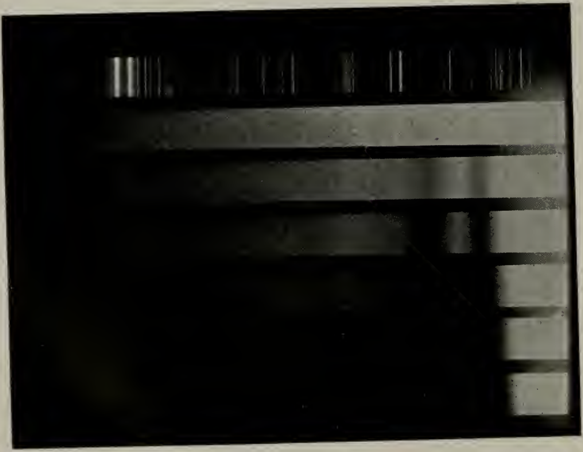

Plate VIII

X.

[illegible] to p. 352.

in turn shaken with an equal volume of 87 per cent. alcohol. From this shaking only 165 cc. carbon disulphide solution remained, but this was made up to 200 cc. with carbon disulphide and then shaken with 200 cc. of 87 per cent. alcohol. These extractions with 87 per cent. alcohol were repeated seven successive times. The carbon disulphide portion was then treated in like manner with 90 per cent. alcohol six times, and finally with 92 per cent. alcohol five times, making twenty-five extractions in all. At every stage of the operation we were guided by the spectroscope. As pointed out in our former paper, the position of the first band of neochlorophyllan in dilute solution is not identical with that of allochlorophyllan and the same is true for the primal substances. The shading on the more refrangible side of this band is due to the allochlorophyll and in this way we could follow the course of the extraction. The neochlorophyll remained in the carbon disulphide solution, whereas the allochlorophyll was removed gradually by the alcoholic extracts.[1] The last carbon disulphide portion was evaporated to dryness on a water bath and the residue taken up in alcohol, filtered, treated with a 10 per cent. alcoholic solution of oxalic acid, and after standing for some hours the neochlorophyllan was filtered off and washed. Plate III represents a photograph of neochlorophyllan in the ultraviolet, obtained by the method just described. Although the prints and reproductions of the spectra of the two neochlorophyllans obtained by different methods are identical yet upon closely scrutinizing the negatives it will be found that the negative of the latter contains a very faint trace of a band in the region of the copper line $\lambda = 437.8$, showing that a trace of allochlorophyllan still remained. The above process was repeated and the extraction with 92 per cent. alcohol carried on a little further, which removed the allochlorophyll altogether. The above establishes that it is possible, by means of organic solvents alone, to separate the two green coloring matters in leaves and to obtain at least one of them in pure condition. Plate II gives the visible spectrum of neochlorophyllan obtained by the method just described and is identical in every detail with Plate I. A few per cent. of allochlorophyllan can, however, be detected in the visible spectrum, when mixed with the neo compound, but the present work has brought out that for the chlorophylls the ultraviolet region is far more delicate.

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[1] It will be seen that the method here described is far more complicated than the one used by Marchlewski and C. A. Schunck (*loc. cit.*). The *Acer platanoides* evidently contained much more of the allochlorophyll than *Ficus repens* used by the authors named. The great difference in the composition of green leaves met with, not only in case of the green, but also of the yellow coloring matters, makes it necessary to change the original method of Sorby according to circumstances.

In our effort to obtain a method for determining one of these coloring matters in the presence of the other we have made use of this fact, and have photographed artificial mixtures of neo- and allochlorophyllan having the following compositions:

Table III

		Neochlorophyllan	Allochlorophyllan
Plate	IV	100 per cent.	0 per cent.
"	V	90 "	+ 10 "
"	VI	80 "	+ 20 "
"	VII	70 "	+ 30 "
"	VIII	60 "	+ 40 "
"	IX	50 "	+ 50 "
"	X	40 "	+ 60 "
"	XI	30 "	+ 70 "
"	XII	20 "	+ 80 "
"	XIII	10 "	+ 90 "
"	XIV	0 "	100 "

A much larger series of photographs could, of course, have been made, thus making the range for estimation smaller, but from the present series it is certainly possible to determine the composition of a mixture to within two per cent. from the prints, and less than that from the negatives.

The method is then to prepare the chlorophyllan from any plant in the ordinary way, being careful to remove all the yellow coloring matters by means of several precipitations with alcohol from concentrated chloroform solutions and to make a solution whose concentration is equal to those photographed in the series, or 0.00004 gram per cc., and then to take a photograph in the ultraviolet, with the same thickness of layers, i. e., 2, 4, 6, 8, 10 and 12 mm. A direct comparison of

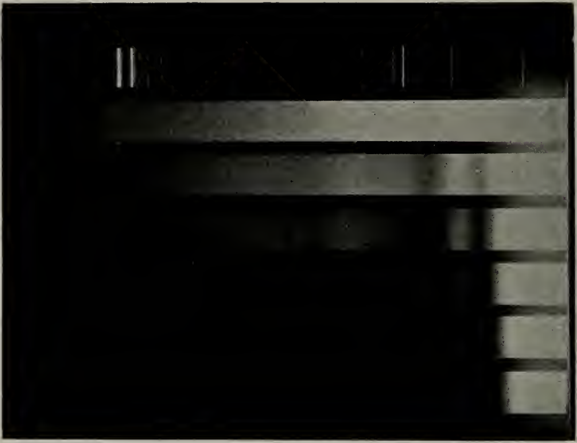

Plate IX

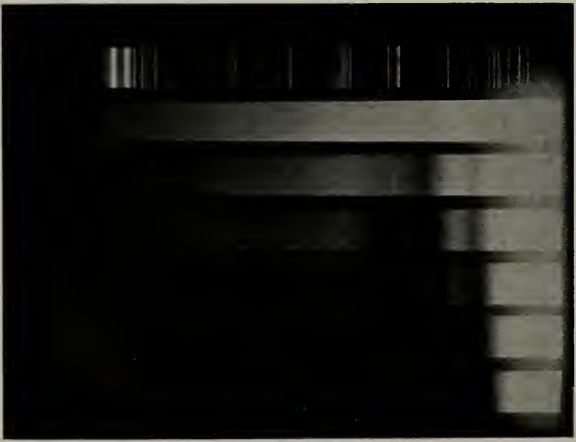

Plate [illegible]

VIII.

see errata

p. 3[illegible]

the photograph with those given in this series will reveal the composition.

An experiment was carried out to ascertain if the yellow coloring matters of the leaves exert an influence on the chlorophyllan bands in the ultraviolet in such small concentrations. To this end 1 liter of alcoholic extract of *Acer platanoides* was divided into two equal portions. One was treated with 15 cc. of 10 per cent. alcoholic oxalic acid and allowed to stand overnight. Calcium carbonate in excess of the oxalic acid was then added, to prevent the formation of phyllocyanin, and the solution evaporated to dryness on the water bath. The residue was extracted with chloroform until the brown color was removed. The chloroform solution measured 302 cc. One cc. of this solution was diluted with chloroform to 60 cc., which was approximately our standard concentration, and the solution photographed in the ultraviolet. It gave a normal chlorophyllan spectrum. To the other portion was added 25 grams solid potassium hydroxide and the solution allowed to stand for two hours with frequent stirring. The solution was then evaporated to a syrup, at a low temperature, on the water bath, after which water was added and the aqueous solution extracted with ether in a separating funnel. Six shakings with ether were required before the latter separated colorless. The ether was distilled off and the yellow coloring matters dissolved in chloroform, filtered and made up to the same volume as the chlorophyllan in the first part of the experiment. The same volume concentration of the yellow coloring matters was then photographed in the ultraviolet. This resulted in a blank negative.

We have thus established that the yellow coloring matters in leaves, the carotin and xanthophylls, do not influence the chlorophyllan bands in the ultraviolet in the proportion in which the two are present in *Acer platanoides* leaves. If this were the case in all other varieties of leaves the method of determining the ratio of neo- to allochlorophyll could be much simplified. It would only be necessary to acidulate the alcoholic extract of the material with oxalic acid, to neutralize the excess of the acid by adding calcium carbonate, to evaporate the solution to dryness, extract the residue with chloroform and to take a series of photographs in the ultraviolet.

The second method for determining the ratio of neo- to allochlorophyllan in mixtures of the two is based on the extinction coefficients of the chloroform solutions. This method has already been applied by Marchlewski and Malarski[1] for determining the total green coloring matter in a given plant. We have already called attention to the difference existing in the green part of the spectrum of neo- and allochlorophyllan and have recorded the extinction coefficients of nettle, *Platanus occidentalis* and *Acer negundo* chlorophyllans, obtained by means of a monochromator, but in that case the light was only approximately monochromatic. For the present work we employed a cadmium lamp giving true monochromatic light in this region of the spectrum. The extinction coefficients were obtained of the same mixtures of neo- and allochlorophyllan as were photographed in the series beginning with neo- and ending with allochlorophyllan. The same spectrophotometer and method for calculating the results were employed as described in our previous paper, to which reference has already been made.

Table IV.—Extinction Coefficients of Artificial Mixtures

Concentration: 0.0004 gram in 1 cc. (chloroform)

Neochlorophyllan	Allochlorophyllan	Cd light $\lambda = 508\ \mu\mu$	Na light $\lambda = 589\ \mu\mu$
100 per cent.	0 per cent.	4.38	1.22
90 “	+ 10 “	4.24	1.34
80 “	+ 20 “	4.14	1.42
70 “	+ 30 “	3.99	1.52
60 “	+ 40 “	3.90	1.61
50 “	+ 50 “	3.80	1.68
40 “	+ 60 “	3.70	1.76
30 “	+ 70 “	3.54	1.85
20 “	+ 80 “	3.41	1.97
10 “	+ 90 “	3.33	2.07
0 “	100 “	3.21	2.16

The above results, obtained with the cadmium light, are represented in the following figure and it will be seen that the curve, barring experimental errors, is a straight line.

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[1] Biochem. Z., **24**, 319.

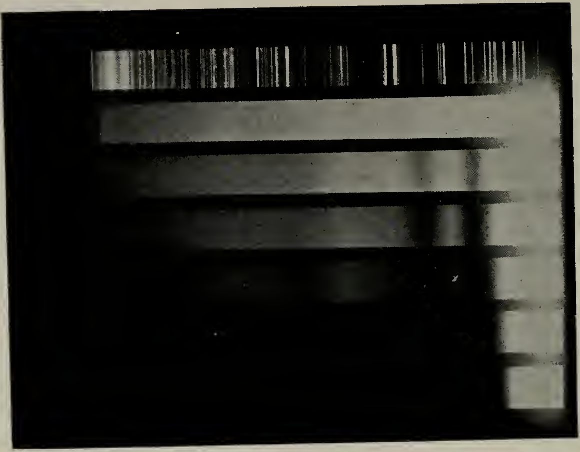

Plate XI

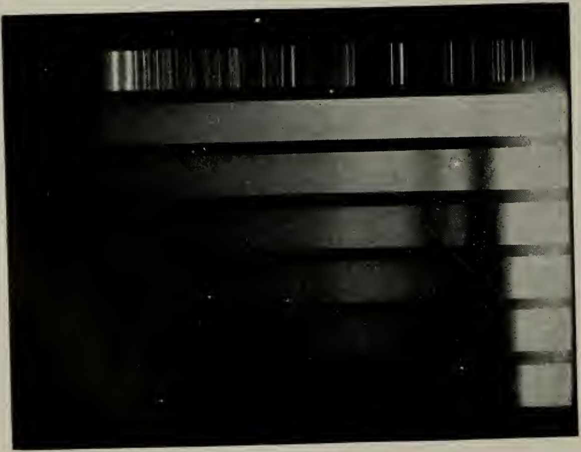

Plate XII

By closely observing the spectra of the two substances in the visible portion it will be seen that the second band of allochlorophyllan extends slightly further in the direction of the more refrangible end than that of the neo compound, so that the edge of the allochlorophyllan band just overlaps the sodium line, while the edge of the neo band does not quite reach it. Consequently we ought to find the reverse arrangement of the extinction coefficients for the above mixtures when sodium light is employed. Our results, given in Table IV, obtained with the sodium light, are embodied in Fig. II, which is self-explanatory. The ordinates of the curves are the extinction

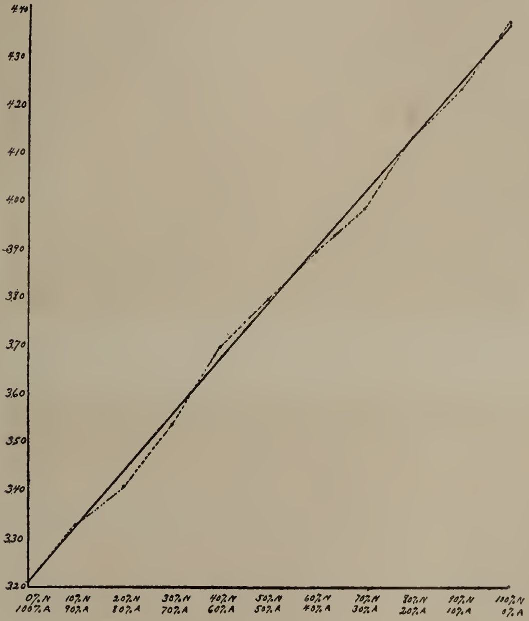

Fig. I

coefficients and the abscissas the percentage composition. *N* represents neochlorophyllan and *A* allochlorophyllan

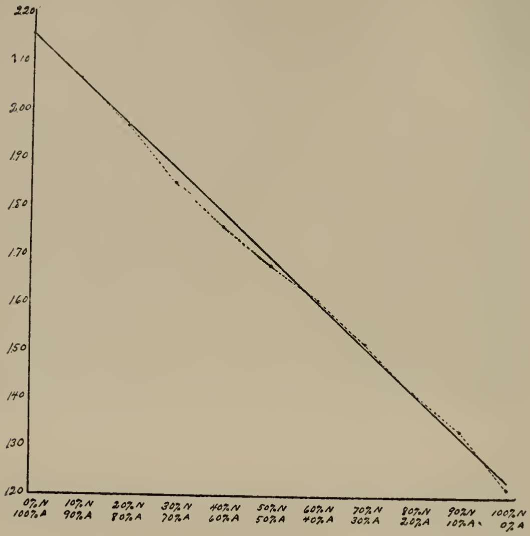

Fig. II

Also in this case it is seen that the percentage composition of any mixture of neo- and allochlorophyllan is a linear function of its extinction coefficient.

The extinction coefficients, either in cadmium or sodium light, therefore furnish a delicate method for determining the ratio of neo- to allochlorophyllan in an unknown mixture, provided the chlorophyllan has been well purified and the concentration standardized with great care. The photographic method is not so sensitive to impurities and is therefore more adapted to practical application.

Chloroform solutions of the following varieties of chlorophyllans have been employed to illustrate the present photo-

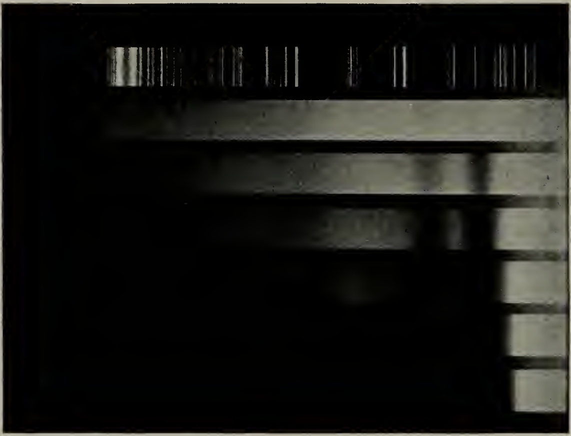

Plate XIII

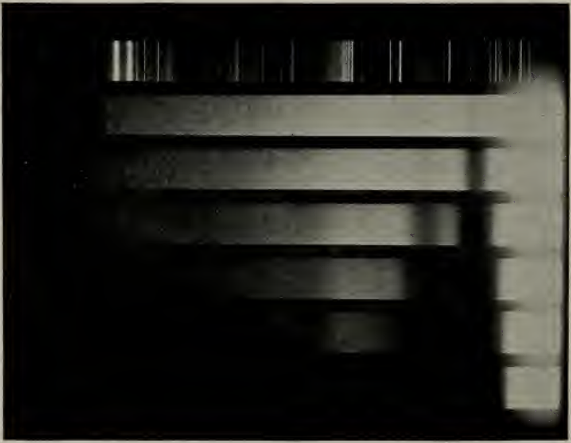

Plate XIV

graphic method of determining the two components. The solutions used, however, have been standing for more than three months, and some have undoubtedly changed in concentration during the time, so we should not expect to find the method by the extinction coefficients to give concordant results, since the curves are made from freshly prepared solutions. The time at our disposal was too short to prepare new solutions of different varieties. A slight change in concentration does not influence the photographic method a great deal because ten times more dilute solutions are employed and the relative intensity of the absorption bands would not be appreciably influenced. The same volume concentration and thickness of layers were used for the unknown solutions as for those in the series. The results were found to be as follows:

Table V

	Neochlorophyllan Per cent.	Allochlorophyllan Per cent.
Nettle (Plate IX of our first series)	72	28
Acer negundo (Plate VI)	12	88
Platanus occidentalis (Plate VIII)	40	60
Acer campestre	58	42
Isatis tinctoria	65	35
Acer pseudo-platanus purpur.	43	57
Fern	63	37
Galeopsis tetrahyt	60	40

In two cases we were able to test the above results by the extinction coefficient method. The *Isatis tinctoria* chlorophyllan gave a coefficient for Cd light of 3.98; by interpolation, using the absorption curve, Fig. I, we find 66 per cent. neochlorophyllan and 44 per cent. allochlorophyllan. The nettle chlorophyllan gave $E = 4.01$, corresponding to 69 per cent. neo- and 31 per cent. allochlorophyllan.

It is then seen that we have here two methods applicable for determining the ratio of the components of chlorophyll. The photographic method can be used when only very small quantities of material are available. Having the comparison series of spectrographs, the determination is easily and quickly made.

The extinction method is more sensitive to colored impurities, but where the quantity of chlorophyll is large enough so that it can be sufficiently purified, this method allows of greater accuracy.

POTENTIALS OF ZINC IN ALCOHOLIC SOLUTIONS OF ZINC CHLORIDE

By Frederick H. Getman and Vernette L. Gibbons

In a previous communication[1] it was pointed out that the potential difference between cadmium and alcoholic solutions of some of its salts is not in accord with the theory of Nernst. The present paper is the second of a series which we hope to publish from time to time as the investigation of the electromotive behavior of the metals in nonaqueous solutions progresses. In it an account is given of our studies on the potential differences between zinc and alcoholic solutions of zinc chloride.

Very little work has been done on potentials of zinc in the alcohols. Kahlenberg[2] measured the potential difference between zinc and zinc chloride in the following combinations:

(A)	(B)	E.M.F.	E.M.F. of (A)
$\overset{-}{\text{Zn}}$—0.05 N $ZnCl_2$ in water. . .	normal electrode	1.082	0.522
$\overset{-}{\text{Zn}}$—0.05 N $ZnCl_2$ in ethyl alc. . . .	normal electrode	0.910	0.350
$\overset{+}{\text{Zn}}$—0.05 N $ZnCl_2$ in ethyl alc. . . .	0.05 N $ZnCl_2$ in water—Zn	0.195	0.327

Jones and Smith[3] determined the electromotive force of the element

Zn—0.1 N $ZnCl_2$ in ethyl alcohol. . 0.1 N $ZnCl_2$ in water—Zn

and found it to be 0.195 volt.

No data for the electrical conductivity of zinc chloride in methyl and ethyl alcohols being available, it was necessary to determine this before proceeding to the study of the electromotive behavior of the metal in these solutions.

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[1] Getman: This Journal, **46**, 117 (1911).

[2] Kahlenberg: J. Physic. Chem., **3**, 379 (1899).

[3] Jones and Smith: This Journal, **23**, 377 (1900).

Electrical Conductivity

Materials Used.—The methyl and ethyl alcohols were obtained from Kahlbaum and were dehydrated for several weeks over lime, after which they were distilled into dry glass-stoppered receivers, the first runnings being discarded. The zinc chloride was obtained from Eimer and Amend and was guaranteed to be pure. It was rendered anhydrous by distilling it in a hard glass tube in a current of dry hydrochloric acid gas, after which the distilled product was immediately transferred to a glass-stoppered weighing bottle and placed in a desiccator over phosphorus pentoxide.

The solutions were made up by direct weighing, the alcohol being freshly distilled and the zinc chloride freshly prepared for each mother solution. Dilutions were made by means of a carefully calibrated burette. Where aqueous solutions were employed, water distilled according to the method of Jones and Mackay was used in making the solutions.

Conductivity Apparatus.—The measurements of electrical conductivity were made by means of Köhler's improved Kohlrausch apparatus. The bridge wire was calibrated by the well known method of Strouhal and Barus. The conductivity cells were of the Arrhenius form, closed by tight-fitting ebonite covers. The constants of these cells were determined by means of 0.02 N potassium chloride, the specific conductivity of which was taken to be 0.002773 reciprocal ohm at 25°. The cell constants were redetermined at frequent intervals. The electrodes of the cells were platinized in the usual manner, it having been demonstrated that the finely divided platinum exerted no appreciable catalytic action during the time of measurement. The electrodes were removed immediately after each measurement to avoid any possible oxidation of the alcohol. The thermostat used to maintain a temperature of 25° was electrically controlled, the maximum temperature variation being about ±0°.05. By means of a bath of melting ice an average temperature of 0°.2 was maintained for conductivity measurements in the neighborhood of 0°. All thermometers used throughout the investigation were calibrated by comparison with a Reichsanstalt standard thermometer. The solutions were allowed to remain in the baths until the conductivity became constant; this required from twenty to thirty minutes.

Results.—In Table I are given the conductivity data for zinc

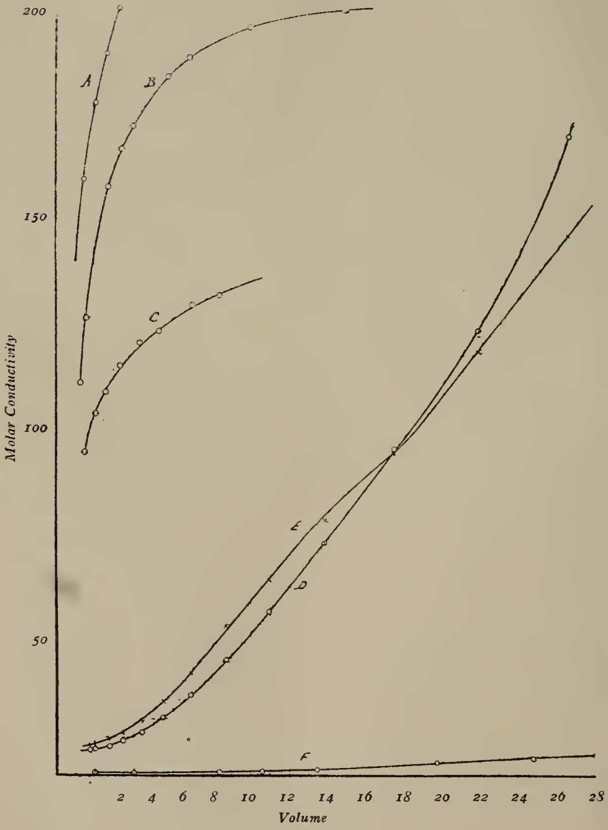

Fig. I

chloride in aqueous solution: m denotes the molar concentration, V is the volume of solution containing one mole, μ_{25° and μ_{0° are the molar conductivities at 25° and 0°, respectively, and β is the temperature coefficient of conductivity. The solutions were diluted by means of two 20 cc. pipettes, one of which was calibrated for capacity and the other for delivery. Dilution was continued until the hydrolysis of the zinc chloride became apparent. The data of Table I are plotted in Fig. I, *A* and *C* being the curves for 25° and 0°. The curve marked *B* was obtained from the work of Kohlrausch[1] on aqueous solutions of zinc chloride at 18°.

Table I.—Zinc Chloride in Water

m	V	μ_{25°	μ_{0°	β
0.2149	4.6533	156.59	85.52	2.84
0.1074	9.3060	176.53	95.136	3.26
0.0537	18.612	189.27	101.15	3.52
0.0269	37.224	201.34	107.58	4.15
0.0134	74.448	213.80	113.16	4.02
0.0067	148.896	221.04	116.44	4.18
0.0034	297.792	227.20	123.47	4.15
0.0017	595.584	238.28	125.95	4.49

The conductivity measurements for the methyl alcohol solutions are recorded in Table II. It will be noticed that with the exception of the most dilute solutions the molar conductivities at 0° are greater than those at 25°, or, in other words, the solutions have negative temperature coefficients. This phenomenon has been observed by Cattaneo[2] for solutions of hydrochloric acid in ether.

To assure ourselves that this abnormal result was not due to the presence of moisture or to some error in the measurements, the experimental work was repeated from the beginning. A fresh portion of methyl alcohol was distilled and a new sample of zinc chloride was prepared, extra precautions being taken to exclude moisture. The values obtained in the second series of measurements agreed within the limits of experimental error with those of the first.

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[1] Kohlrausch: Wied. Ann., **26**, 161 (1885).

[2] Cattaneo: Rend. r. accad. Lincei, [5] **2**, 295.

The results recorded in Table II are plotted as curves *D* and *E* in Fig. I.

Table II.—Zinc Chloride in Methyl Alcohol

m	V	μ_{25°	μ_{0°	β
0.1982	5.0948	6.8098	7.9034	—0.0437
0.0991	10.1897	6.9437	8.3638	—0.0568
0.0496	20.3793	7.6590	9.5329	—0.0749
0.0248	40.7586	8.9748	11.3102	—0.0934
0.0124	81.5172	11.282	14.346	—0.1225
0.00620	163.034	15.108	19.508	—0.1760
0.00310	326.069	21.131	27.208	—0.2431
0.00155	652.138	30.562	37.815	—0.2901
0.000775	1304.275	42.105	51.65	—0.3418
0.000387	2608.550	61.351	67.511	—0.2464
0.000194	5217.101	85.718	84.720	+0.0399
0.000097	10434.202	116.800	104.180	+0.5048
0.000048	20868.403	173.95	141.056	+1.3157

As will be seen, the curves differ decidedly from those obtained with aqueous solutions. As the dilution increases the curve for 25° crosses the curve for 0° and beyond this point they show a tendency to assume the form *A*, *B* and *C*. This abnormality in the conductivity curves is ascribed to association of the zinc chloride in solution, this phenomenon having been observed by Jones and his coworkers[1] and by one of us in connection with our work on solutions of cadmium iodide in methyl and ethyl alcohols.[2] That zinc chloride is associated in alcoholic solutions is shown by subsequent determinations of its molecular weight in methyl and ethyl alcohols.

From the fact that the molecular conductivities of the more concentrated solutions in methyl alcohol at 0° are smaller than the molecular conductivities at 25° we infer that the complex formed at the lower temperature is not identical with the complex in solution at the higher temperature.

The results obtained with ethyl alcohol solutions are recorded in Table III:

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[1] Jones: Z. physik. Chem., **62**, 41 (1908). Kreider and Jones: This Journal, **45**, 282 (1911).

[2] Getman: *Loc. cit.*

Table III.—Zinc Chloride in Ethyl Alcohol

m	V	μ_{25°	μ_{0°	β
0.1316	7.5979	0.3219	0.2018	0.0048
0.0658	15.1957	0.3242	0.1990	0.0050
0.0329	30.3914	0.3255	0.2119	0.0045
0.0263	37.9893	0.3013	0.1995	0.0041
0.0165	60.7829	0.3236	0.2136	0.0044
0.0132	75.9786	0.3384	0.2197	0.0048
0.00823	121.5658	0.3773	0.2439	0.0053
0.00628	151.9572	0.3947	0.2619	0.0053
0.00411	243.1315	0.4968	0.3150	0.0073
0.00329	302.9144	0.5296	0.3435	0.0074
0.00206	486.2630	0.5606	0.3685	0.0077
0.00165	605.8288	0.7207	0.4593	0.0105
0.000823	1211.6576	1.0756	0.6538	0.0169
0.000411	2423.3152	1.5209	1.0495	0.0189
0.000263	3798.967	2.4311	1.5959	0.0334
0.000206	4846.630	2.2922	1.7165	0.0232
0.000132	7597.934	3.5986	2.5483	0.0420
0.000066	15195.868	4.4225	2.9892	0.0573

The vertical scale of Fig. I being too small to admit of representing the conductivity in ethyl alcohol at 0° and 25°, the data for the higher temperature alone are plotted at *F*; while in Fig. II the data for the two temperatures are plotted on a larger vertical scale.

Here the conductivities at 0° lie below those at 25°, but the form of the curves is much the same as with methyl alcohol. Again we attribute this departure from the normal conductivity curve to association of the solute.

Molecular Weight Determinations.—In order to confirm the supposition that zinc chloride is associated in the alcoholic solutions molecular weight determinations were made by means of the boiling point method. The results are given in Table IV:

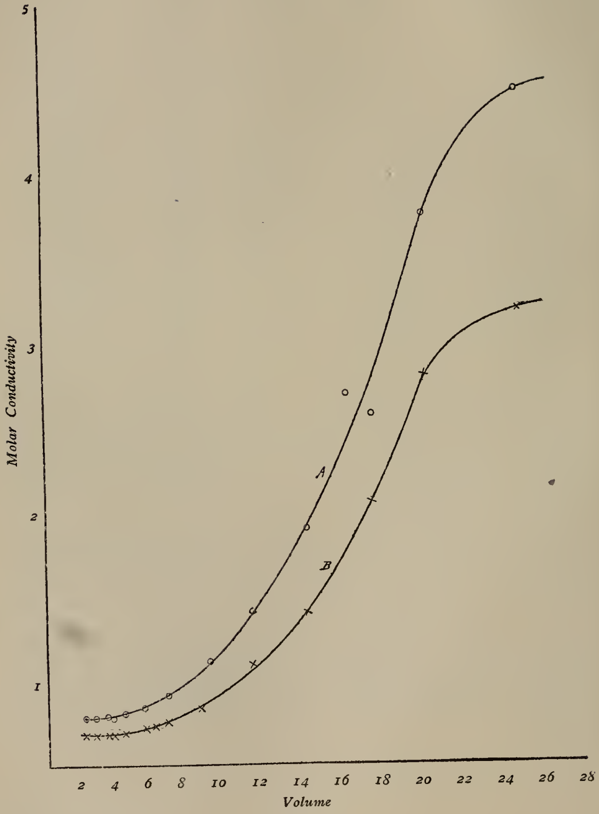
5
4
3
2
1
Molar Conductivity
A
B
2
4
6
8
10
12
14
16
18
20
22
24
26
28
Volume

Fig. II

Table IV.—Molecular Weight of Zinc Chloride

Solvent: CH_3OH		Solvent: C_2H_5OH	
Molar concentration	Molecular weight	Molar concentration	Molecular weight
0.2	190.7	0.214	149.4
0.2	198.2	0.214	155.8
0.2	187.2	0.107	146.9
0.2	200.8	0.107	148.9
Mean,	194.2	Mean,	150.2

The molecular weight of zinc chloride as calculated from the formula is 136.43. The above results show that the solute is associated in both solvents, the association in methyl alcohol being greater than in ethyl alcohol.

Electrode Potentials

Apparatus.—The apparatus used in this investigation was similar to that employed in our previous work on cadmium in alcoholic solutions with the exception of the electrode vessels, a sketch of which is given in Fig. III. The vessel A contained the solution and the zinc electrode E. By means of the side tube and rubber tube, I, connection was established with the other vessel, B, which served as the calomel electrode. The

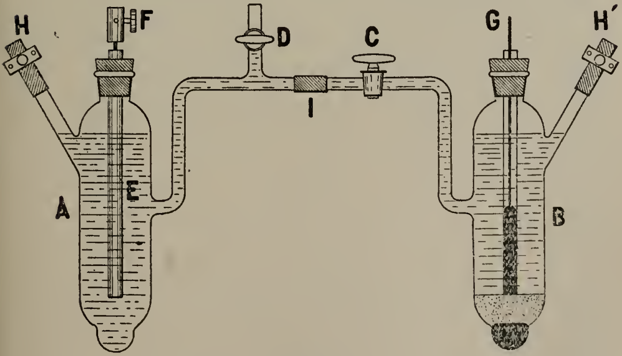

Fig. III

connecting tube was filled with solution by opening the stopcocks C and D and blowing gently through a glass tube inserted in the rubber tubing at H′, the screw pinchcock at this point being opened. The pressure of the air forces some of the N potassium chloride solution from the calomel electrode through C and I, any air bubbles escaping at D. The stopcocks were now closed, as was also the pinchcock H′, and the experimental cell was introduced into the circuit by means of the connections F and G.

The zinc electrode, E, was made by casting Baker & Adamson's purest zinc in the form of a cylindrical rod 5 mm. in diameter and 8 cm. long, after which a stout copper wire and connector was soldered to one end.

The surface of the zinc was cleaned by immersion in dilute acid and subsequent washing in distilled water. Before inserting the electrode in the solution, the surface was thoroughly amalgamated.

Two cells were employed, one being placed in the 25° bath while the other was maintained at 0°, as in the measurement of the electrical conductivity of the solutions.

After the cells had acquired the temperature of the bath the stopcock C was opened just long enough to determine the point of balance on the bridge wire. By keeping C closed except when making measurements, diffusion is minimized. As in our previous work, we have assumed that any electromotive force which may be set up at the junction of the solutions is negligible.

Results.—The electrode potentials in aqueous solutions were found to follow Nernst's law provided the concentration was above 0.1 molar.

In less concentrated solutions the electrode potential becomes steadily smaller, instead of increasing (i. e., becoming more negative) as Nernst's law requires. This anomalous behavior in dilute solutions led us to repeat these determinations with great care, with the result that in the second series of measurements the potentials were again too small but widely divergent from the values obtained in the first series for the same concentrations. The electrode potentials were found to vary with time, but the variation was so erratic as to preclude any explanation based upon progressive changes in the solutions or on the electrodes. In a paper on the electrometric method for the determination of hydrolysis, Denham[1] encountered similar difficulties with aqueous solutions of zinc chloride and states that the potential fluctuated most erratically over a period of four weeks, when further measurements were abandoned. As a result of his observations he suggests that the phenomenon may be due to the formation of colloidal substances which interfere with the normal course of hydrolysis.

The observed values of the electrode potentials at 0° and 25° are given in Table V, together with the values of the potentials calculated by means of the equation

$$\pi_1 = \pi_0 + \frac{RT}{nF} \log_e \frac{m_1\mu_1}{m_0\mu_0}$$

where π_1 and π_0 are the electrode potentials corresponding to solutions of molar concentrations m_1 and m_0, and molar conductivities μ_1 and μ_0. The symbols R, T, F and n have their usual significance. The electrode potential in the most concentrated solution is taken as π_0 in calculating the other potentials.

Table V.—Zinc Chloride in Water

m	μ_{25}	μ_0	$\pi_{25°}$ (obs.)	$\pi_{25°}$ (calc.)	$\pi_{0°}$ (obs.)	$\pi_{0°}$ (calc.)
0.3010	155.0	84.5	—0.509	—0.509	—0.525	—0.525
0.21488	156.6	85.5	—0.511	—0.513	—0.526	—0.529
0.16116	168.0	91.0	—0.514	—0.515	—0.527	—0.532
0.10744	176.5	95.1	—0.518	—0.520	—0.527	—0.536

The data of Table V are plotted in Fig. IV. Logarithms of $m\mu$, being proportional to the ionic concentrations, are chosen as abscissas and electrode potentials as ordinates. A and B represent electrode potentials as a function of ionic concentration at 25° and 0°, while C represents the results of Labendzinski[2] on the electrode potentials of zinc in aqueous zinc chloride solutions, presumably at 25°, although this author does not mention the temperature at which he worked. It will be observed that in every case the calculated potentials are slightly greater than the experimental values.

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[1] Denham: J. Chem. Soc., **93**, 41 (1908).

[2] Labendzinski: Z. Elektrochem., **10**, 77 (1904).

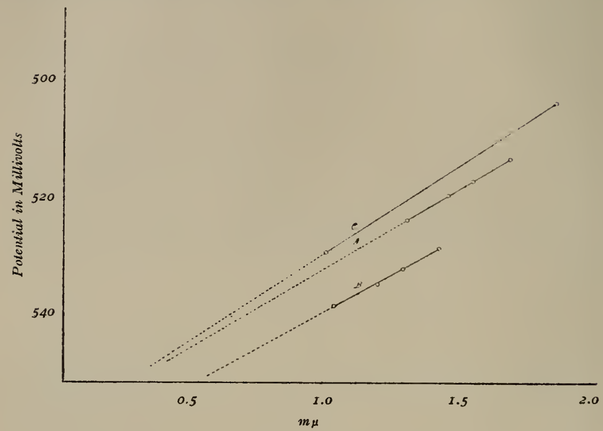

Fig. IV

The individual measurements are accurate to within two millivolts, so that where the difference between the observed and calculated potentials exceeds this value, the error must be ascribed to some source other than the method employed in making the measurements.

The dotted portions of the curves *A*, *B* and *C* may be used to obtain by extrapolation the values of the electrode potentials in the more dilute solutions where the experimental data are untrustworthy.

From the data of Table V it is possible to calculate the heat of ionization of zinc by means of the equation of Helmholtz,

$$\pi = \frac{Q}{nF} + T\frac{d\pi}{dT}$$

where π is the electrode potential of zinc in a molar solution of zinc ions, Q is the heat produced when one gram equivalent of zinc passes from the metallic to the ionic state, and F, T

and n have their usual significance. Rearranging the equation, we have:

$$Q = \left(\pi - T\frac{d\pi}{dT}\right)nF$$

To determine the value of π, we make use of the Nernst equation,

$$\pi_1 = \pi_0 + 0.0295 \log \frac{m_1\mu_1}{m_0\mu_0}$$

Taking $\pi_0 = -0.509$ volt and $\mu_1 = 115$ (conductivity of molar zinc chloride at 25°),

$$\pi_1 = -0.509 + 0.0295 \log \frac{115}{0.301 \times 155}$$

$$\pi_1 = -0.497 \text{ volt}$$

Substituting this value in the Helmholtz equation, we have

$$Q = (-0.497 - 298 \times 0.000664)(2 \times 96540 \times 0.2394) = 32120 \text{ cal.}$$

This value compares well with the following results obtained by Ostwald[1] and Jahn:[2]

	Ostwald	Jahn	G. and G.	Mean
Heat of ionization of zinc (calc.)	32600	33950	32120	32890

The data for zinc chloride in methyl alcohol solutions are given in the following table:

Table VI.—Zinc Chloride in Methyl Alcohol

m	$\pi_{25°}$	$\pi_{0°}$	m	$\pi_{25°}$	$\pi_{0°}$
0.2000	—0.366	—0.382	0.0542	—0.402	—0.410
0.1750	—0.409	—0.424	0.0257	—0.410	—0.426
0.1500	—0.434	—0.447	0.0103	—0.430	—0.451
0.1250	—0.393	—0.418	0.0021	—0.409	—0.426
0.1029	—0.415	—0.418	0.0001	—0.419	—0.447
0.0750	—0.434	—0.460			

An inspection of this table will show that the electrode potentials fluctuated over a range of more than a centivolt, a variation much larger than the experimental error. This somewhat anomalous behavior of zinc in methyl alcohol solutions of zinc chloride is being studied in this laboratory at the present time and will be made the subject of a future paper.

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[1] Ostwald: Z. physik. Chem., **11,** 501 (1893).

[2] Jahn: *Ibid.,* **18,** 399 (1895).

The change in potential of the zinc electrode in solutions of zinc chloride in ethyl alcohol is very uniform, as will be seen from Table VII and Fig. V, curve *A* representing the potentials at 25° and Curve *B* those at 0°:

Table VII.—Zinc Chloride in Ethyl Alcohol

m	$\pi_{25°}$	$\pi_{0°}$	m	$\pi_{25°}$	$\pi_{0°}$
0.2138	—0.399	—0.407	0.0535	—0.352	—0.388
0.1604	—0.383	—0.398	0.0268	—0.340	—0.385
0.1069	—0.366	—0.396	0.0134	—0.337	—0.378
0.0800	—0.354	—0.388			

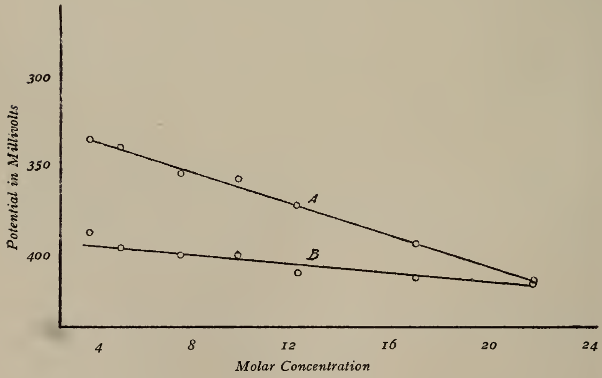

Fig. V

The abnormality of the conductivity curves for solutions of zinc chloride in ethyl alcohol (Fig. II) renders uncertain any calculation of the degree of ionization of the solute, hence in representing graphically the data of the foregoing table we have plotted molar concentrations as abscissas instead of attempting to plot ionic concentrations as in Fig. IV. The electrode potential is nearly a linear function of the molar concentration, the slope of the line being dependent upon the temperature. If this linear relation holds for solutions of greater concentration than those with which we have worked a reversal of temperature coefficients must occur, solutions of concentration above 0.24 molar having positive instead of negative coefficients.

The value of the electrode potential diminishes with dilution instead of increasing as in aqueous solutions. This is in agreement with the results obtained by one of us[1] in our investigation of the behavior of the cadmium electrode in alcoholic solutions of cadmium salts. A comparison of our results with those of Kahlenberg[2] for solutions of approximately the same concentration is of interest as a check on the accuracy of the measurements. He found for a 0.05 molar solution of zinc chloride in ethyl alcohol at room temperature an electrode potential of —0.350 volt while we obtain for a 0.0535 molar solution at 25° a potential of —0.352 volt, the agreement being most satisfactory.

In view of the abnormal conductivities of solutions of zinc chloride in ethyl alcohol and the inverse variation of electrode potential with concentration in these solutions, it is obvious that any attempt to calculate the solution pressure of zinc in ethyl alcohol would be futile.

SUMMARY

(1) The electrical conductivities of solutions of zinc chloride in water, methyl alcohol and ethyl alcohol have been measured. The conductivities in aqueous solutions are normal while those in alcoholic solutions give evidence of association of the solute and also of possible complex formation between solute and solvent. The more concentrated solutions in methyl alcohol have negative temperature coefficients.

(2) Molecular weight determinations by the boiling point method have shown that in both alcohols zinc chloride is associated, the association in methyl alcohol being greater than in ethyl alcohol.

(3) The potentials of zinc in aqueous and alcoholic solu-

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[1] Getman: *Loc. cit.*

[2] Kahlenberg: *Loc. cit.*

tions of zinc chloride have been determined by measuring the electromotive force of the combination

$$\text{Zn–Sol. ZnCl}_2\text{—Calomel Electrode}$$

and deducting $0.56 + 0.0006t$, the potential of the calomel electrode. The electrode potential of zinc in aqueous solutions has been shown to follow Nernst's law in the more concentrated solutions, but in the dilute solutions the experimentally determined potentials are much smaller than the calculated.

The potentials in methyl alcohol solutions oscillate over a range of more than ten millivolts. This variation is being made the subject of a special investigation.

Zinc in ethyl alcohol solutions gives with decreasing concentration a uniformly diminishing potential, this behavior being the reverse of that in aqueous solutions.

Bryn Mawr College
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A STUDY OF THE REFRACTIVE INDICES OF SOLUTIONS OF THE CADMIUM HALIDES

By Frederick H. Getman and Helen T. Gilroy

The refractive indices of solutions of the halides of cadmium have been measured by several investigators.[1] After reviewing the work of these experimenters and having noted some lack of agreement between the results it seemed desirable to redetermine with great care the refractive indices and densities of solutions of cadmium chloride, cadmium bromide and cadmium iodide.

Materials Used.—The salts used in this investigation were prepared by the Hoffmann & Kropff Chemical Company, and were guaranteed to be pure. The solutions were made up with conductivity water having a mean specific conductivity of 1.5×10^{-6} reciprocal ohms. The salts were dehydrated by prolonged confinement in a desiccator over concentrated sulphuric acid and subsequent heating to constant weight. The solutions were prepared by direct weighing of both salt and solvent, the concentrations being expressed in per cent. of salt.

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[1] Bender: Wied. Ann., **39,** 89 (1890). Barbier and LeRoux: Compt. rend., **110,** 458 (1890). Jahn: Wied. Ann., **43,** 280 (1891). De Muynck: *Ibid.*, **53,** 561 (1894). Gladstone and Hibbert: J. Chem. Soc., **67,** 831 (1895). Le Blanc and Rohland: Z. physik. Chem., **19,** 282 (1896). Hallwachs: Wied. Ann., **68,** 30 (1899).

Apparatus and Method.—The densities of the solutions were determined in a Sprengel-Ostwald pyknometer of approximately 6 cc. capacity. The pyknometer was suspended in a thermostat maintained at 25° (±0°.1) for about fifteen minutes, after which its contents were adjusted so that the meniscus was tangent to the mark on the stem. The densities were calculated by the familiar formula

$$d_{4^\circ}^{25^\circ} = \frac{W_1}{W_2}(Q - \lambda) + \lambda$$

where

$d_{4^\circ}^{25^\circ}$ = density of solution at 25° referred to water at 4°
W_1 = weight of solution
W_2 = weight of an equal volume of water
Q = density of water at 25° = 0.99707

and

λ = mean density of air = 0.0012

The refractive indices were measured with the improved form of Pulfrich refractometer manufactured by Zeiss and furnished with a Van Aubel thermostat. The temperature of the solution and prism could be maintained at 25° (±0°.1) for several hours, thus minimizing an error which has been more or less indeterminate in some of the earlier investigations on refractive indices. The refractive index of each solution has been measured for the *D* line of sodium and for the *C* and *F* lines of hydrogen.

Before proceeding to make any measurements with the refractometer the error of the zero reading of the instrument was determined and all subsequent readings were corrected. In addition to the correction of the zero of the instrument correction for the temperature of the prism was applied, these two corrections insuring an accuracy in the refractive indices of two units in the fifth place of decimals.

Before entering upon the study of the solutions the refractive index of the water used as a solvent was determined with great care. The mean of several determinations of the refractive index for the *D* line was 1.33250, which agrees very well with the value, 1.33248, recently found by Baxter, Burgess and Daudt[1] as the result of a special investigation of the refractive index of water.

To insure the solutions having acquired the temperature of the thermostat and to prevent changes in concentration due to evaporation of the solvent, the cell of the refractometer was closed by means of the tight-fitting rim of the heating vessel and the solution allowed to stand for thirty minutes before taking any readings.

Results.—The formula of Lorentz[2] and Lorenz[3] was used in calculating the specific refractions of the solutions, it being generally conceded that the values obtained by the use of this formula are more nearly constant under varying conditions than the values given by the Gladstone and Dale or other empirical relations.

As Baxter and his coworkers[4] have pointed out, none of the formulas for specific refraction are entirely satisfactory and consequently any relationship which is dependent upon specific refraction is more or less uncertain.

We have assumed that the specific refractions of solute and solvent are additive and have calculated the specific refraction of the salt from the specific refractions of the solution and water according to the formula

$$r = \frac{1}{p}\left(\frac{n^2 - 1}{n^2 + 2}\cdot\frac{100}{d} - \frac{n^2_W - 1}{n^2_W + 2}\cdot\frac{100 - p}{d_W}\right)$$

where r = specific refraction of salt in solution
p = per cent. of salt
n = index of refraction of solution at 25°
n_W = index of refraction of solvent at 25°
d = density of solution at 25°
and d_W = density of water at 25°

In the tables which follow p, d and r have the same significance as above, while n_C, n_D and n_F denote the indices of refraction for the C, D, and F lines and M is the molecular weight of the solute.

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[1] Baxter, Burgess and Daudt: J. Am. Chem. Soc., **33**, 893 (1911).

[2] Lorentz: Wied. Ann., **9**, 642 (1880).

[3] Lorenz: *Ibid.*, **11**, 70 (1880).

[4] Baxter, Boylston, Mueller, Black and Goode: J. Am. Chem. Soc., **33**, 901 (1911).

Table I.—Cadmium Chloride in Water (25°)

p	d	n_C	n_D	n_F	$\frac{n^2-1}{n^2+2} \cdot \frac{1}{d}$	r	Mr
1.599	1.0115	1.33325	1.33517	1.33935	0.2045	0.1063	19.48
4.472	1.0368	1.33755	1.33929	1.34361	0.2018	0.1118	20.48
8.620	1.0695	1.34292	1.34499	1.34935	0.1985	0.1195	21.91
11.600	1.1068	1.34858	1.35088	1.35522	0.1948	0.1086	19.91
18.690	1.1803	1.36110	1.36316	1.36811	0.1885	0.1124	20.60
21.201	1.2165	1.36615	1.36833	1.37326	0.1851	0.1071	19.63
26.076	1.2700	1.37631	1.37850	1.38380	0.1818	0.1127	20.66
31.090	1.3401	1.38681	1.38925	1.39473	0.1756	0.1081	19.82
41.540	1.5153	1.41436	1.41710	1.42333	0.1662	0.1103	20.21
						Mean,	20.30

Table II.—Cadmium Bromide in Water (25°)

p	d	n_C	n_D	n_F	$\frac{n^2-1}{n^2+2} \cdot \frac{1}{d}$	r	Mr
1.05	1.0059	1.33043	1.33330	1.33891	0.2049	0.1047	28.49
2.76	1.0212	1.33430	1.33623	1.34038	0.2032	0.1015	27.63
5.41	1.0470	1.33834	1.34001	1.34458	0.2002	0.0980	26.68
11.03	1.1016	1.34599	1.34782	1.35247	0.1902	0.1047	28.49
15.66	1.1509	1.35308	1.35500	1.36008	0.1893	0.0990	26.95
21.13	1.2133	1.36213	1.36425	1.36965	0.1840	0.1017	27.68
27.51	1.2991	1.37381	1.37624	1.38184	0.1767	0.0996	27.11
40.74	1.4918	1.40130	1.40373	1.41063	0.1639	0.1026	27.93
						Mean,	27.62

Table III.—Cadmium Iodide in Water (25°)

p	d	n_C	n_D	n_F	$\frac{n^2-1}{n^2+2}\cdot\frac{1}{d}$	r	Mr
0.834	1.0042	1.33186	1.33368	1.33804	0.2052	0.1079	39.52
3.340	1.0249	1.33548	1.33714	1.34151	0.2030	0.1108	40.56
3.880	1.0303	1.33547	1.33780	1.34193	0.2023	0.1109	40.60
6.984	1.0581	1.34021	1.34228	1.34699	0.1993	0.1103	40.38
13.491	1.1216	1.35049	1.35258	1.35706	0.1932	0.1112	40.71
20.133	1.1933	1.36167	1.36435	1.37007	0.1869	0.1113	40.75
26.785	1.2780	1.37553	1.37839	1.38508	0.1805	0.1105	40.46
39.860	1.4801	1.40798	1.41104	1.41952	0.1678	0.1101	40.32
						Mean,	40.41

Summary of Results

It will be observed on inspection of the foregoing tables that the specific and, consequently, the molecular refractions are nearly constant over the entire range of concentrations, the slight variations in the specific refractions being greatly magnified when these are multiplied by the molecular weights of the respective salts. It seems justifiable to select the mean of the molecular refractions of the solutions of each salt as a close approximation to its true molecular refraction.

In their paper on the refractive indices of aqueous solutions of the halogen salts of lithium, sodium and potassium, Baxter and his students[1] have computed the atomic refractions of the constituents of the salts studied, assuming the value of the atomic refraction of hydrogen to be 1.03.

The following table gives the mean values of the atomic refractions as calculated by Baxter:

Table IV

Hydrogen	1.03	Lithium	1.27
Chlorine	7.50	Sodium	1.75
Bromine	11.05	Potassium	3.24
Iodine	17.68		

Taking the values for the atomic refractions of chlorine, bromine and iodine as here given, we may calculate the atomic refraction of cadmium from the mean values of the molecular refractions of its halogen salts, thus:

20.30 (mol. ref. $CdCl_2$) —15 (2 × at. ref. Cl) = 5.30 at. ref. Cd
27.62 (mol. ref. $CdBr_2$)—22.1 (2 × at. ref. Br) = 5.52 at. ref. Cd
40.41 (mol. ref. CdI_2) —35.36 (2 × at. ref. I) = 5.05 at. ref. Cd

Mean, 5.29

While it would be unwise to attempt to formulate any generalization from such a limited amount of data it is of interest to review very briefly some of the facts which must be considered when such a generalization is established.

Gladstone[2] has shown that the product of the specific refraction and the square root of the equivalent weight of an element is a constant the value of which for univalent metals is approximately 1.30 and for polyvalent metals about 1.01, these values being computed from specific refractions derived by means of the Gladstone and Dale formula. This relation between valence and specific refraction suggests a connection between refraction and volume, it having been pointed out by Traube,[1] LeBas,[2] and Barlow and Pope[3] that there exists a simple relationship between valence and volume. Further evidence of the existence of some relation between refraction and volume has been furnished by Traube,[4] who has shown that b, the volume factor in van der Waals' equation, is about 3.5 times as large as the molecular refraction calculated by means of the Lorentz-Lorenz formula. Exner[5] has pointed out that the molecular refraction of a compound calculated by means of the Lorentz-Lorenz formula is nearly proportional to the volume occupied by the atoms. On the assumption that molecular refraction is a measure of the nuclear volumes of the atoms in a substance, Traube has shown that in a series of carbon compounds of various classes the ratio of the molecular refraction to the total number of valences of the constituent atoms is a constant. This constant he terms the refraction stere.

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[1] *Loc. cit.*

[2] Gladstone: P. Roy. Soc., **60**, 140 (1896).

If the sum of the external volumes of the atoms is represented by b in van der Waals' equation and the nuclear volume is represented by Mr then $b—Mr$ must be a measure of the atomic volumes and the ratio of $b—Mr$ to n, the total number of valences, will represent what Traube calls the valon stere. Traube defines a valon as an active group of electrons occupying the covolume, the active electrons endowing the atom with valence. The valon steres for a series of hydrocarbons, amines and esters are found to approximate to a constant value.

All of the above relations fail to apply to the halides of lithium, sodium, potassium and cadmium, but since these substances are so different in chemical character from those studied by Traube it could hardly be expected that the same relationships would be found to apply, at least without some modification.

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[1] Traube: Ber. d. chem. Ges., **40**, 130, 723, 734 (1907).

[2] Le Bas: J. Chem. Soc., **91**, 112 (1907).

[3] Barlow and Pope: *Ibid.*, **89**, 1675 (1906); **91**, 1150 (1907).

[4] Traube: Drude's Ann., **5**, 552 (1901).

[5] Exner: Wien. Ber., **91**, 85 (1885).

Richards[1] has shown that there is a close relationship between the atomic volumes of the elements and their compressibilities. If the compressibilities of the elements are plotted against their atomic weights the curve obtained indicates that one is a periodic function of the other.

Hauke[2] has studied the relation between the specific refractions and the atomic weights of the elements and he finds it to be periodic, the specific refraction increasing to a maximum at the middle of each period and diminishing towards the end.

In the following table are given the values of the atomic volumes, the atomic refractions and the compressibilities of the elements mentioned above:

Table V

Element	At. vol.	At. refr.	Comp.
Lithium	13.1	1.27	8.8
Sodium	23.7	1.75	15.4
Potassium	45.5	3.84	31.5
Cadmium	13.0	5.29	1.9

While there is no self-evident mathematical relation connecting these various magnitudes yet there is evidently some underlying principle which, when discovered, will make possible the expression of atomic refraction in terms of such quantities as atomic volume, compressibility and valence.

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A STUDY OF THE CHANGE FROM VIOLET TO GREEN IN SOLUTIONS OF CHROMIUM SULPHATE

By Minnie A. Graham

INTRODUCTION

In 1841 Schrötter,[3] while studying a series of compounds formed by sulphuric acid and chromic oxide, observed the existence of one of the products in two varieties. From a solution of anhydrous chromic sulphate in sulphuric acid, he obtained, by precipitation with alcohol, a light violet, crystalline salt, which resembled chrome alum. In accordance with his analytical results, he represented this salt by the formula

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[1] Richards: Z. Elektrochem., **13,** 519 (1907).

[2] Hauke: Wien. Ber., **105,** IIA, 749 (1896).

[3] Pogg. Ann., **53,** 513 (1841).

$$Cr_2O_3 + 3SO_3 + 15H_2O$$

The green filtrate from the violet salt, on evaporation, left a green amorphous substance which he regarded as another form of chromic sulphate. He concluded that there were two modifications of the solution of neutral chromic sulphate, from one of which he had obtained the violet salt and from the other the green substance.

Schrötter also observed that a solution of the violet compound became green when heated to 70°, and attributed this change in color to loss of water. Krüger[1] afterwards observed the same change and proved that the green solution contained free acid.

Since the time of Schrötter and Krüger this interesting phenomenon has been a favorite subject of investigation. Favre and Valson[2] showed that only a fraction of the sulphate ion in the green solution is precipitated by barium chloride, and they assumed that the remainder forms a complex with the chromium. Recoura,[3] on the other hand, decided that the green solution contains free acid and a sulphate formed in accordance with the equation

$$2Cr_2(SO_4)_3 + H_2O = [Cr_4(SO_4)_4O]SO_4 + H_2SO_4$$

and that the precipitated barium sulphate obtained by Favre and Valson was derived in part from the salt and in part from the free acid. From results obtained by thermochemical measurements, Recoura concluded that one molecule of free acid is present in the green solution of two molecules of chromic sulphate.

[1] Pogg. Ann., **61**, 218 (1843).

[2] Compt. rend., **74**, 1016 (1872).

[3] Ann. chim. phys., [7] **4**, 494 (1895).

Whitney,[1] in 1896, found that the electrical conductivity of the green solution is much greater than that of the violet solution of the same concentration, and attributed this difference to the presence of free acid in the green solution. He found also that addition of alkali to the green solution at first decreases the conductivity and that this decrease ceases when one molecule of sodium hydroxide has been added for each molecule of chromium sulphate in the original solution, further addition of the base increasing the conductivity. This diminution in conductivity is evidently due to neutralization of free acid by the base. This is in agreement with the conclusion of Recoura[2] previously referred to. The conductivity of the violet solution is only slightly diminished and soon begins to increase when sodium hydroxide is added. Whitney[3] later confirmed the presence of free acid in the green solutions by means of experiments on the velocity of ionic migration.

In 1903 Richards and Bonnet[4] undertook the determination of the amount of free acid in the solutions by measuring the extent of the inversion produced in solutions of cane sugar by solutions of chromium sulphate. They also carried out experiments in dialysis and neutralization which indicated the presence of free acid in the solutions, and by measurements of ionic migration they showed that there is present no anion containing chromium and, therefore, no ionized complex acid such as $HCr(SO_4)_2$, which some investigators have assumed to be formed.

Denham,[5] a few years later, made a careful study of the degree of hydrolysis in both solutions by means of measurements of the potential of cells made up in the following form:

I. H_2—violet solution—calomel electrode, and
II. H_2—green solution—calomel electrode

He concluded that the hydrolysis of the normal violet chromium sulphate is somewhat greater than that of aluminium sulphate; that the green salt contains a complex cation and may be represented by the formula

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[1] Z. physik. Chem., **20**, 40 (1896).

[2] *Loc. cit.*

[3] J. Am. Chem. Soc., **21**, 1078 (1899).

[4] Z. physik. Chem., **47**, 29 (1904).

[5] Z. anorg. Chem., **57**, 361 (1908).

$$[Cr_4(SO_4)_4](SO_4)_2$$

that this salt is strongly hydrolyzed in solution according to the equations:

$$\text{I. } [Cr_4(SO_4)_4](SO_4)_2 + 2H_2O = [Cr_4(SO_4)_4]SO_4(OH)_2 + H_2SO_4$$

$$\text{II. } [Cr_4(SO_4)_4](SO_4)_2 + 4H_2O = [Cr_4(SO_4)_4](OH)_4 + 2H_2SO_4$$

Equation I represents concentrated solutions and Equation II dilute solutions.

It will be seen from this brief historical survey that the problem under investigation has been attacked in a variety of ways and with different objects in view. The principal physico-chemical methods that have been applied, heretofore, are those used in the measurement of dialysis, electrical conductivity, potential, catalytic inversion of sugar, depression of the freezing point and ionic migration. In the present investigation, the purpose has been to study more closely the conditions under which the color change takes place and the variation in the properties of the solutions that accompany this change of color, and, also, to determine, if possible, the degree of hydrolysis in the two solutions.

With this end in view, I measured the density, viscosity and electrical conductivity of both the violet and green solutions, studied the catalytic effect of these solutions on the inversion of sugar, and photographed the absorption spectra of both solutions through a wide range of concentrations.

The Preparation of Violet Chromium Sulphate

For the purpose of the research, it was necessary to prepare a sufficient supply of pure chromium sulphate in its violet modification. The method of Traube,[1] as modified by Richards and Bonnet,[2] seemed more satisfactory than others and was accordingly followed. This consists in the reduction, by means of alcohol, of chromic acid in solution in water and sulphuric acid. Richards and Bonnet found that by careful cooling and slow addition of alcohol the yield of violet salt was much increased. Preliminary to the preparation of a larger quantity the work of Richards and Bonnet was followed, using twenty grams of chromic acid and thirty grams of pure sulphuric acid dissolved in sixty grams of water. This preparation required nearly three days and yielded fourteen grams of the violet salt. The quantities of chromic acid, sulphuric acid and water were then increased ten-fold, the resulting solution was cooled to —5° in a freezing mixture and reduced with 95 per cent. alcohol that had been cooled in an ice chest. The alcohol was added very slowly from a dropping funnel while the solution was constantly agitated, the temperature being kept as low as possible—approximately 8°—though occasionally, because of the heat evolved in the reduction, it went a little above 10°. Alcohol was added at intervals until a quantity sufficient for the reduction had been used. Very little solid separated from the solution during the first 24 hours; but when the mixture was allowed to stand out of doors at a temperature of about 5° for 17 hours longer, it deposited a heavy green precipitate. Further addition of cold alcohol to the solution, the beaker being surrounded by a freezing mixture, produced no appreciable rise in temperature, indicating that the reduction was complete. The precipitate, when filtered upon a Buchner funnel and washed with cold alcohol, appeared grayish green by daylight and lavender by electric light. It was dissolved in the smallest possible quantity of pure ice-water, giving a deep blue solution with a tendency to become green at room temperature. To this blue solution cold absolute alcohol was added and a light violet, crystalline precipitate with a pearly luster was obtained, which was filtered, washed sparingly with absolute alcohol, and further purified by solution in ice-water and reprecipitation with absolute alcohol. The final product was not washed, but dried as thoroughly as possible between layers of filter paper, and finally placed in a large desiccator containing sticks of potassium hydroxide. In the moist condition the product shows a tendency to become green at room temperature; but after thorough drying a violet powder, apparently stable in the air, is obtained. This preparation gave a yield of seventy-seven grams, and required nearly five days for its completion. A year later, when another preparation was necessary, special care was taken to control the conditions so as to increase the yield if possible. As previous results seemed to indicate that time is an important factor in the formation of the salt, the solution was left in an ice chest for intervals of several hours between successive additions of alcohol. The alcohol was added so slowly that the temperature never rose above 10°, and for the greater part of the time it was kept as low as 5°, the solution being cooled to 0° or —3° during the intervals between additions. In the process of purification all solutions were kept as cold as the solubility of the salt permitted, and the desiccator containing the final product was kept in an ice chest. This preparation took ten days and yielded one hundred and seventy grams, the initial solution having been made from two hundred grams of chromic acid, three hundred grams of sulphuric acid and six hundred grams of water. It would be interesting to study more thoroughly the influence of time upon the yield, as it was observed that the cooled filtrates, upon standing, deposited considerable quantities of the violet salt, and it is possible that the yield might be still further increased by allowing more time for deposition.

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[1] Ann. Chem. (Liebig), **66**, 88 (1848).

[2] *Loc. cit.*

Analyses

The violet salt was analyzed for chromium by ignition to the oxide.

I. 1.0738 grams of salt gave 0.2381 gram Cr_2O_3.
II. 0.8806 gram of salt gave 0.1958 gram Cr_2O_3.

	Calculated for $Cr_2(SO_4)_3.16H_2O$	Found I	II
Cr_2O_3	22.33	22.17	22.24

The sulphuric acid in the same salt was determined by precipitation with barium chloride, care being taken to avoid occlusion of chromium compounds. Barium sulphate was precipitated from a cold solution of the salt, to which hydrochloric acid had been added, and the mixture was thoroughly boiled before filtration.

I. 0.5810 gram of salt gave 0.5877 gram $BaSO_4$.
II. 0.6213 gram of salt gave 0.6308 gram $BaSO_4$.

	Calculated for $Cr_2(SO_4)_3.16H_2O$	Found I	Found II
SO_3	35.30	34.69	34.86

	Calculated for $Cr_2(SO_4)_3.16H_2O$	Found (by difference)
H_2O	42.36	43.00

For each gram molecule of chromic oxide there were found to be 2.96 gram molecules of sulphuric acid, expressed as sulphur trioxide, indicating that the salt is normal. The water was found by difference to be 43.00 per cent., corresponding to 16.36 H_2O. Varying amounts of water have been assigned to the salt by different investigators. It is probable that the salt loses water when kept in a desiccator, although no change in the appearance of the dried salt has been observed. A specimen dried entirely in the air gave a value of 22.35 per cent. for chromic oxide, while a small quantity dried in a vacuum desiccator gave 23.59 per cent.—the value calculated for $Cr_2(SO_4)_3.14H_2O$. Other specimens, left for a long time in the potassium hydroxide desiccator, gave values of 23.72 and 23.64 per cent. of chromic oxide, indicating a loss of water after long standing over potassium hydroxide.

Density of Solutions

The first property to be studied quantitatively was the density of solutions. In the preparation of solutions the weight of violet salt calculated for a given concentration was dissolved in pure ice-water in a graduated flask; the solution was allowed to reach room temperature, and then diluted to the mark. The weight of salt was calculated on the basis of the formula $Cr_2(SO_4)_3.16H_2O$, and the concentration of the chromium was afterwards determined by evaporating a definite volume of the solution and igniting the residue. The solutions exhibit a rich violet color by transmitted light, and a deep blue surface color. Experience has shown that the solutions gradually lose their violet color at room temperature and become greenish blue. Although the amount of hydrolysis at this temperature may not seriously affect the physico-chemical measurements to be made, it was thought best to keep the solutions in an ice chest.

For the determination of density a Sprengel-Ostwald pycnometer, having a volume of approximately twenty cubic centimeters, was employed for temperatures between 20° and 95°, and a Reischauer specific gravity flask, of about the same volume, with a long graduated neck, for temperatures below 20°. These were calibrated with water for the desired ranges of temperature and a curve plotted for use in the calculation of the density of the solutions at different temperatures. A large beaker served as bath, the pycnometer or flask being suspended in the bath long enough for the temperature of the liquid to become constant, then brought to the temperature of the balance and weighed. A constancy of 0°.1 was possible during these determinations. The same method was followed in weighing the chromium solutions: a solution of violet salt was introduced into the pycnometer, kept in the bath for a sufficient length of time to insure constancy of temperature, and then weighed. The temperature of the bath was raised five or ten degrees and the pycnometer again suspended, no change being made in the solution except as it became necessary to add or remove a small quantity in order to adjust the volume to the fixed mark of the pycnometer. As the temperature was raised the blue solution was observed to change gradually in appearance and between 40° and 50° it became decidedly green. The temperature was carried to 90° or 95°, the values calculated from the weights being taken as the density of the violet solution at the different temperatures. The bath was then cooled five or ten degrees at a time, and the pycnometer containing the solution was weighed for successive temperatures as before. The values calculated from these observations are taken as the density of the green solution with varying temperature. It was noticed that above 90° water evaporated from the green solution and so, in general, the determinations were not made beyond this temperature.

The densities were calculated from the usual expression,

$$d_4^{t°} = \frac{w_s}{w_a}(Q - L) + L$$

where d represents the density of the solution; w_s the apparent weight of the solution in air; w_a the weight of an equal volume of water; Q the specific gravity of water at temperature t; and $L = 0.0012$, the mean density of air with reference to water at 4°. The values obtained are given in the following tables:

Table I.—Density

0.1024 Molar Solution

Violet		Green	
Temp.	***d***	**Temp.**	***d***
0°	1.0394	95°	0.9973
4°.5	1.0392	90°	1.0017
10°	1.0391	85°	1.0039
15°	1.0380	80°	1.0089
20°	1.0369	75°	1.0112
25°	1.0362	70°	1.0159
30°	1.0342	65°	1.0175
40°	1.0292	60°	1.0190
50°	1.0242	55°	1.0226
60°	1.0192	50°	1.0279
70°	1.0152	40°	1.0314
75°	1.0102	30°	1.0366
80°	1.0076	25°	1.0382
85°	1.0031	20°	1.0392
90°	1.0007	15°	1.0403
		10°	1.0409
		0°	1.0414

0.1617 Molar Solution

Violet		Green	
Temp.	***d***	**Temp.**	***d***
0°.5	1.0612	95°	1.0162
9°.5	1.0602	90°	1.0202
15°	1.0592	85°	1.0232
20°	1.0585	80°	1.0252
25°	1.0572	75°	1.0292
30°	1.0552	70°	1.0322
40°	1.0512	65°	1.0352
50°	1.0462	60°	1.0382
55°	1.0432	55°	1.0412
60°	1.0412	50°	1.0432
65°	1.0372	40°	1.0482
70°	1.0342	30°	1.0512
75°	1.0312		
80°	1.0262		
85°	1.0232		
90°	1.0192		

Table I—(Continued)

0.2137 Molar Solution

Violet Temp.	d	Green Temp.	d
20°	1.0763	85°	1.0377
25°	1.0744	75°	1.0440
30°	1.0728	65°	1.0505
40°	1.0680	55°	1.0552
50°	1.0628		
60°	1.0551		
70°	1.0493		

0.3221 Molar Solution

Violet Temp.	d	Green Temp.	d
21°	1.1152	85°	1.0722
25°	1.1132	80°	1.0772
30°	1.1102	75°	1.0802
40°	1.1062	70°	1.0832
50°	1.1002	65°	1.0872
55°	1.0962	60°	1.0912
60°	1.0922	55°	1.0932
65°	1.0872	50°	1.0972
70°	1.0842	40°	1.1032
75°	1.0802	30°	1.1092
80°	1.0762	25°	1.1112
85°	1.0712	21°	1.1122
90°	1.0692		

Table II.—Density

Molar conc. of violet sol.	d $t = 0°$	d $t = 10°$	d $t = 20°$	d $t = 30°$	d $t = 40°$
0.1024	1.0394	1.0391	1.0369	1.0342	1.0292
0.1617	1.0617	1.0602	1.0585	1.0552	1.0512
0.2137	....	....	1.0763	1.0728	1.0680
0.3221	....	....	1.1160	1.1102	1.1062
	$t = 50°$	$t = 60°$	$t = 70°$	$t = 80°$	$t = 90°$
0.1024	1.0242	1.0192	1.0152	1.0076	1.0007
0.1617	1.0462	1.0407	1.0342	1.0262	1.0192
0.2137	1.0628	1.0551	1.0493	....	....
0.3221	1.1002	1.0922	1.0842	1.0762	1.0692

These results show that with few exceptions the violet solutions are of greater density than the green solutions of the same concentration. These exceptions are, in general, among the values obtained at high temperatures and are most marked for the solutions heated above 90°. In the solution of lowest concentration the densities of the two forms are approximately the same. Where the values for the green exceed those for the violet it is undoubtedly due to the fact that at the higher temperatures the solution lost water and, consequently, the green solution had a greater concentration than the violet.

The changes in density with varying temperature are shown in Fig. I and the changes with varying concentration in Fig. II, full lines representing the violet, and broken lines the green solutions. Since, in Fig. II, the lines showing change of density with change of concentration are nearly parallel, straight lines, it appeared justifiable, by extrapolation, to obtain values for the density of a fifth solution not measured experimentally.

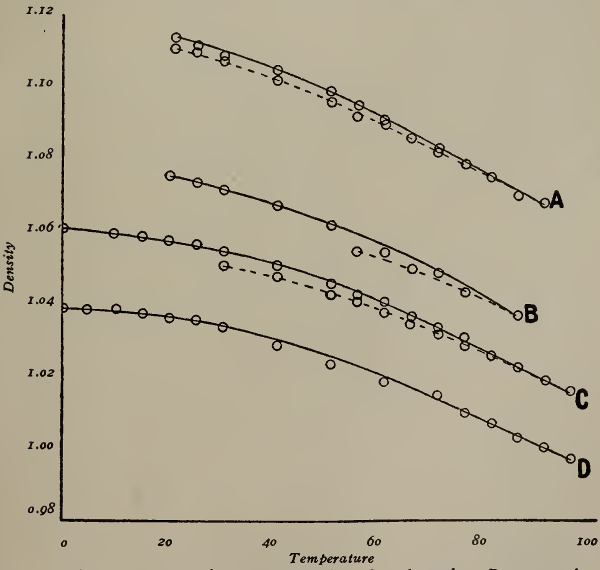

Fig. I. A, 0.3221 molar. B, 0.2137 molar. C, 0.1617 molar. D, 0.1024 molar.

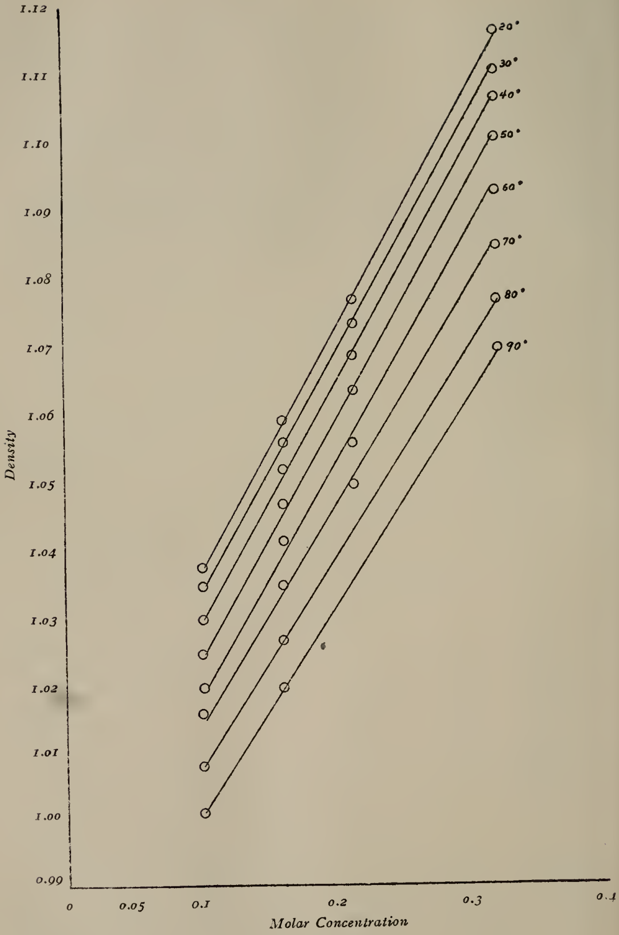
1.12
1.11
1.10
1.09
1.08
1.07
1.06
1.05
1.04
1.03
1.02
1.01
1.00
0.99
Density
0
0.05
0.1
0.2
0.3
0.4
Molar Concentration
20°
30°
40°
50°
60°
70°
80°
90°

Fig. II

The curve plotted from these values is similar to those of Fig. I.

It is evident that there is no point of temperature or concentration where the density of the solutions changes suddenly, since all values for both violet and green solutions lie on smooth curves.

Viscosity

The solutions used in the measurement of viscosity were those whose densities had been determined. In these measurements the Poiseuille-Ostwald method was employed, which consists in observing, with a stopwatch, the time of flow of a definite volume of liquid, under its own pressure, between two marks on a capillary tube. Two tubes of the Ostwald-Poiseuille type were used for this purpose, a constant for each tube being determined by measuring the time of flow of a definite volume of pure water. The constants were measured at 20° and calculated from the formula,

$$K = \eta/dt$$

where t is the time of transpiration in seconds, $\eta = 0.01002$,[1] the coefficient of viscosity of water at 20°, and $d = 0.998230$,[1] the corresponding density. In measuring the viscosity of the chromium solutions a volume of the violet solution equal to the volume of water was introduced into the dry tube, and the time of flow measured as before. The coefficient of viscosity was calculated from the expression, $\eta = Kdt$, where η is the coefficient of viscosity of the solution; K, the constant of the tube; d, the density of the solution at the temperature of observation; and t, the time of transpiration in seconds.

In place of the usual thermostat a glass battery jar on a suitable stand was used for securing constant temperatures. An incandescent lamp, connected through a rheostat with an electric light circuit, served to heat the water, which was stirred by a paddle wheel run by a small electric motor. For the observations at low temperatures ice was used in the water of the bath. The tubes were clamped vertically near the center of the battery jar with the level of the water above the upper

[1] Tables of Landolt and Börnstein.

mark of the capillary. An electric light behind the stand served to illuminate the bath and was an aid in making the observations. Accurately graduated thermometers reading to tenths of a degree were used and carefully observed during each series of measurements. At temperatures in the neighborhood of 20° it was possible to keep the bath constant to within 0°.1, but at higher and lower temperatures this was difficult. In all determinations a series of readings was made, the temperature being read to hundredths of a degree for each measurement of the time of transpiration. The average temperature and average time were then used in the calculation of the coefficient. In general, observations were begun at the low temperatures and the bath was gradually heated in the manner described in connection with the determinations of density. Between 40° and 50° a decided change of color was noted and with falling temperature the solution did not regain its violet color. This was observed particularly in this part of the work because the electric light behind the thin layer of liquid in the capillary tube brought out the violet color more clearly.

Table III.—Viscosity

0.0501 Molar Solution

Violet		Green	
Temp.	$\eta \times 10^3$	Temp.	$\eta \times 10^3$
8°	16.78	83°	3.73
10°	15.77	78°	3.95
12°	14.82	75°	4.09
15°	13.61	70°	4.38
18°	12.69	65°	4.63
20°	11.98	60°.7	5.00
25°	10.62	55°	5.32
30°	9.55	50°	5.89
40°	7.76	40°	6.88
50°	6.40	30°	8.53
60°	5.57	25°	9.46
70°	4.87	20°	10.65
77°	4.03	18°	11.19
80°	3.91	15°	12.05
		12°	13.14
		10°	14.03
		7°.8	14.91

Table III—(Continued)

0.1024 Molar Solution

Violet		Green	
Temp.	$\eta \times 10^3$	Temp.	$\eta \times 10^3$
3°.5	17.27	75°	4.23
20°	12.00	70°	4.53
25°	10.65	60°	5.24
30°	9.53	50°	6.13
40°	7.74	40°	7.34
50°	6.43	30°	8.98
60°	5.34	25°	10.06
70°	4.71	20°	11.34
		15°	13.03
		10°	14.93
		5°.3	17.30

0.1617 Molar Solution

Violet		Green	
Temp.	$\eta \times 10^3$	Temp.	$\eta \times 10^3$
3°.4	21.84	77°.9	4.97
5°.8	20.26	75°.8	4.99
9°.4	18.15	70°	5.42
12°.6	16.53	65°	5.81
15°	15.46	59°.8	6.33
20°	13.55	50°	7.44
25°	12.02	40°	9.05
30°	10.76	30°	11.27
40°	8.74	25°	12.54
50°	7.87		
60°	6.59		
63°.3	6.19		
67°	5.83		
75°.9	5.12		

0.2137 Molar Solution

Violet		Green	
Temp.	$\eta \times 10^3$	Temp.	$\eta \times 10^3$
7°.7	21.62	77°.6	4.80
8°.5	21.13	70°.4	5.27
9°.6	20.54	60°.6	6.04
10°.4	20.02	50°	7.23
20°	15.39	40°	8.69
25°	13.96	30°	10.74
30°	12.06	25°	12.00
40°	9.75	20°	13.57
50°	7.95	14°	15.84
55°	7.05	13°.3	16.40
60°	6.43		
69°.7	5.51		

Table III—(Continued)

0.3221 Molar Solution

Violet		Green	
Temp.	$\eta \times 10^3$	Temp.	$\eta \times 10^3$
8°	28.94	83°	5.43
10°	27.05	80°	5.89
12°	25.63	75°	6.27
15°	23.53	70°	6.72
18°	21.87	60°	7.42
20°	20.72	50°	9.07
25°	18.27	40°	11.29
30°	16.21	30°	14.18
40°	13.01	25°	15.90
50°	10.41	20°	17.36
60°	8.47	18°	18.96
70°	7.26	15°	20.65
75°	6.27	12°	22.80
		10°	24.08

Table IV.—Viscosity

Molar conc. of violet sol.	$\eta \times 10^3$ $t = 10°$	$\eta \times 10^3$ $t = 20°$	$\eta \times 10^3$ $t = 25°$	$\eta \times 10^3$ $t = 30°$
0.0501	15.77	11.98	10.62	9.55
0.1024	...	12.0	10.65	9.53
0.1617	18.15	13.55	12.02	10.76
0.2137	20.28	15.39	13.96	12.06
0.3221	27.05	20.72	18.27	16.21
	$t = 40°$	$t = 50°$	$t = 60°$	$t = 70°$
0.0501	7.76	6.40	5.57	4.87
0.1024	7.74	6.43	5.34	4.71
0.1617	8.74	7.87	6.59	....
0.2137	9.75	7.95	6.43	5.69
0.3221	13.01	10.41	8.47	7.26

In calculating the values for the coefficient of viscosity the curves plotted for density at different temperatures were used. As might be expectecd from the relative densities of the two solutions, the green has less viscosity than the violet except at high temperatures, where the values are approximately the same. The change of viscosity with change of temperature is shown in Fig. III, and the change with varying concentration in Fig. IV. In Fig. III two of the solutions have been omitted to avoid confusion, because of the coincidence in each

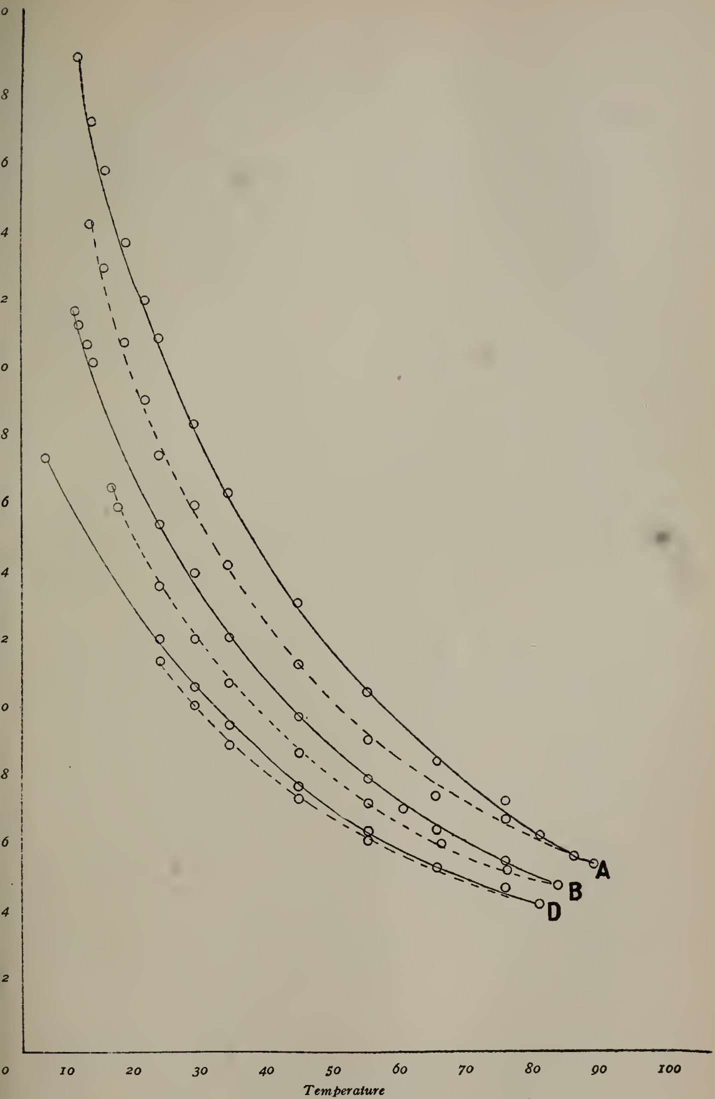

Fig. III. A, 0.3221 mol. B, 0.2137 mol. D, 0.1024 mol.

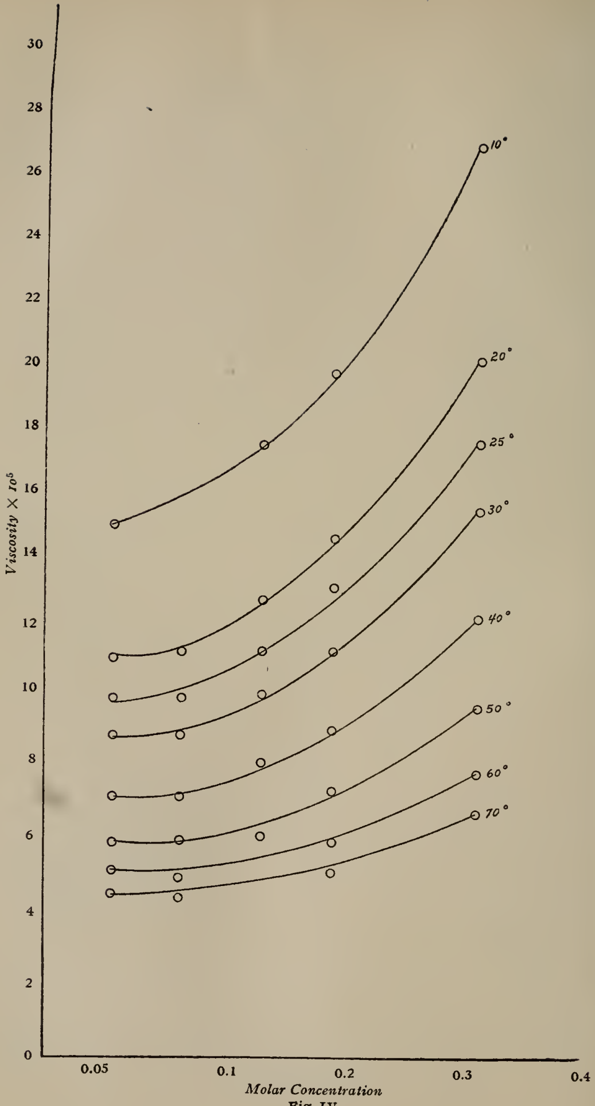
30
28
26
24
22
20
18
16
14
12
10
8
6
4
2
0
Viscosity × 10⁵
0.05
0.1
0.2
0.3
0.4
Molar Concentration
10°
20°
25°
30°
40°
50°
60°
70°

Fig. IV

case of the curve for the violet solution with that of the green of another concentration. The curves omitted are like the others.

The curves for variations in viscosity, like those representing the densities, indicate a gradual change in the solutions with no abrupt transformation at any point. They are similar to those for violet and green solutions of chrome alum given by d'Arcey[1] in his paper on the viscosity of solutions, while the experimental results are in agreement with the conclusion of Ferrero[2] that the difference in viscosity of the two solutions of chrome alum becomes less as the solutions are diluted.

It was hoped that measurements of viscosity might furnish some evidence as to the rate of the reverse change from green to violet and, accordingly, after one series of measurements at different temperatures the tube was heated at 98° for several minutes and the time of flow then measured at 25° from day to day. It was only after one week that a change of one second in time of transpiration could be measured with any certainty and a second week seemed to give no measurable change.

Electrical Conductivity

The conductivity measurements were made by the method of Kohlrausch, the bridge wire having been calibrated as recommended by Strouhal and Barus. A cell of the Arrhenius type, with rather widely separated platinized electrodes, was used, and the cell constant was frequently determined by measuring the conductivity of a fiftieth-molar solution of potassium chloride. All solutions were made with water that was distilled according to the method of Jones and Mackay[3] and had a specific conductivity of 1.35×10^{-6}. For work at low temperatures the cell was immersed in a battery jar filled with snow or ice, and for higher temperatures in a large thermostat heated by an incandescent bulb dipped into the bath, or, when necessary, by a gas flame underneath it. By vigorous stirring with a paddle wheel run by a motor it was possible to keep the temperature constant to 0°.1.

[1] Phil. Mag., [5] **28**, 230 (1889).

[2] Nuovo Cimento, [5] **1**, 285 (1901).

[3] THIS JOURNAL, **19**, 91 (1897).

For the determinations of changes in conductivity with change of temperature a violet solution of definite concentration was placed in the cell and allowed to stand in the thermostat for some time to ensure thermal equilibrium. A series of readings was then made with different resistances in the circuit and the temperature of the bath raised to the next point desired, and the process repeated until a temperature of 60° was reached. The values obtained in this way were taken to represent the conductivity of the violet solution.

Allowing the solution to remain in the cell, the bath was cooled gradually to approximately the initial temperature, and a series of observations made to obtain values for the conductivity of the green solution.

The results obtained for both solutions are given in the following tables:

Table V.—Molecular Conductivity

$v = 4680.3$ cc.

Violet		Green	
Temp.	μ	Temp.	μ
2°.5	59.36	60°.0	151.5
9°.8	72.18	55°.0	149.6
10°.8	74.2	50°.0	146.9
18°.0	92.08	40°.0	136.1
20°.0	93.21	30°.0	121.6
25°.0	101.2	25°.0	114.4
30°.0	110.6	20°.0	105.7
40°.0	125.7	18°.0	102.3
50°.0	137.6	10°.4	89.95
55°.0	143.5	0°.3	72.02

$v = 6185.6$ cc.

Violet		Green	
Temp.	μ	Temp.	μ
0°.3	77.82	60°.0	177.7
9°.3	88.47	50°.0	168.6
14°.5	98.77	40°.0	155.2
18°.0	105.2	30°.0	139.2
20°.0	109.3	25°.0	130.3
25°.0	118.9	20°.0	121.1
30°.0	128.0	18°.0	116.8
40°.0	145.3	15°.0	111.4
50°.0	159.9	11°.2	104.0
		5°.6	91.94
		2°.0	86.10

Table V—(Continued)

$v = 9765.6$ cc.

Violet		Green	
Temp.	μ	Temp.	μ
0°.2	71.88	60°.0	187.9
9°.8	92.52	50°.0	178.9
20°.0	116.05	40°.0	162.7
25°.0	126.13	30°.0	149.2
30°.0	137.15	25°.0	140.1
40°.0	155.9	20°.0	130.6
50°.0	171.6	9°.9	111.57
		0°.0	92.79

$v = 19964.05$ cc.

Violet		Green	
Temp.	μ	Temp.	μ
5°.0	93.93	60°.0	215.9
7°.8	103.6	50°.0	210.5
10°.5	111.0	40°.0	184.0
12°.0	114.4	30°.0	167.4
14°.8	119.5	25°.0	160.3
18°.0	127.8	20°.0	149.7
20°.0	131.5	18°.0	139.6
25°.0	143.5	15°.0	134.8
30°.0	154.8	11°.6	130.3
40°.0	178.7	9°.8	124.4
50°.0	189.3	7°.8	115.9
		5°.0	111.5

Table VI.—Molecular Conductivity

Violet Solution

v (cc.)	μ	μ	μ	μ
	$t = 10°$	$t = 20°$	$t = 25°$	$t = 30°$
4680.3	72.18	93.21	101.2	110.6
6185.6	88.47	109.3	118.9	128.0
9765.6	92.52	116.05	126.13	137.15
19964.05	111.0	131.5	143.5	154.18
	$t = 40°$	$t = 50°$	$t = 60°$	
4680.3	125.7	137.6	151.5	
6185.6	145.3	159.9	177.7	
9765.6	155.9	171.6	187.9	
19964.05	178.7	189.3	215.9	

Table VI—(Continued)

Green Solution

v (cc.)	μ $t = 10°.5$	μ $t = 20°$	μ $t = 25°$
4680.3	88.0	105.7	114.4
6185.6	102.0	121.1	130.3
9765.6	111.57	130.6	140.1
19964.05	124.4	149.7	160.3
	$t = 30°$	$t = 40°$	$t = 50°$
4680.3	121.6	136.1	146.9
6185.6	139.2	155.2	168.6
9765.6	149.2	162.7	178.9
19964.05	167.4	184.0	210.5

Curves showing the changes in molecular conductivity with temperature are plotted in Fig. V, and those showing change in molecular conductivity with change in volume in Fig. VI. The conductivity of the green solution is for all temperatures and all concentrations higher than that of the corresponding violet solution.

As the solutions had not been heated to as high a temperature as in the density and viscosity experiments, two of the solutions were afterwards heated in closed flasks in a bath of boiling water for fifteen minutes and the conductivity then measured at 20°. The value obtained was considerably higher than the first value for the green solution at 20°. The conductivity of this solution slowly dropped when it was kept at 20°. The decrease was perceptible after a few hours and became more marked as the observations were continued. An attempt was made to apply one of the kinetic equations to establish the order of the reverse reaction, but the values calculated for a constant were not satisfactory. The investigation of this feature of the problem has not been continued, but it is hoped that by using the improved method of preparing the green solutions which was adopted later it will be possible to secure some interesting data on the change of green solutions to violet.

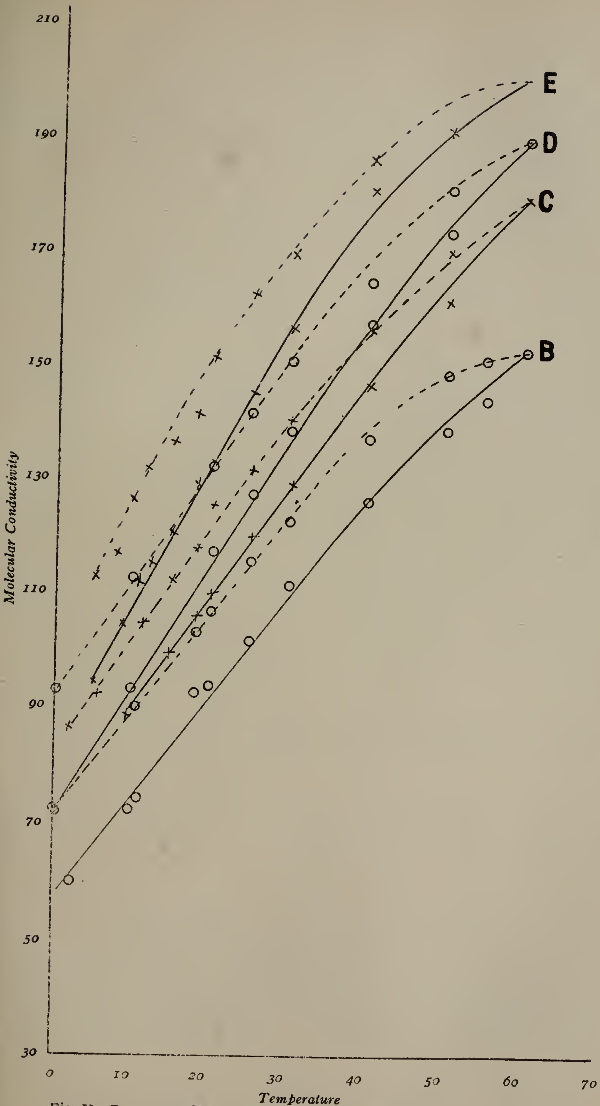

Fig. V. B, 0.2137 molar. C, 0.1617 molar. D, 0.1024 molar. E, 0.0501 molar.

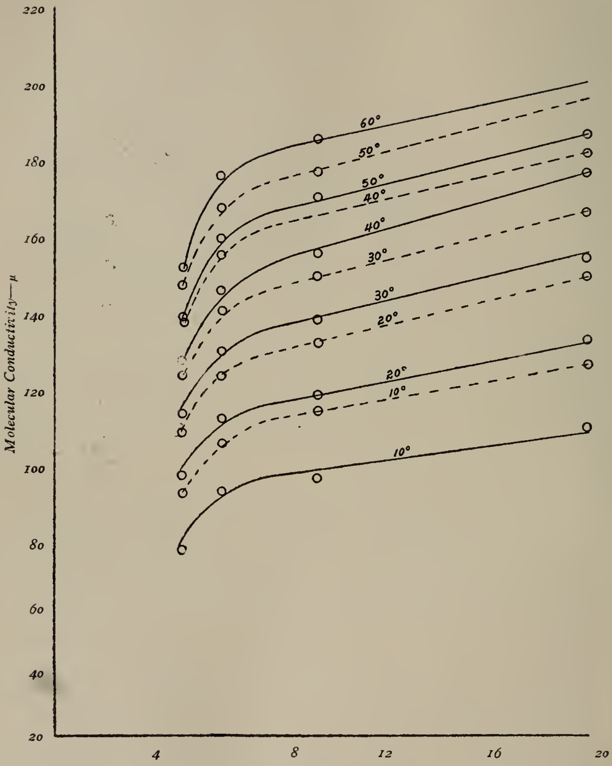

Fig. VI

Conductivity as a Measure of Hydrolysis

For the purpose of determining the extent of hydrolysis of both violet and green solutions very careful determinations were carried out at 0° and 25°. The solutions were kept in special thermostats in which the temperature could be accurately controlled. Each thermostat consisted of two concentric galvanized iron tanks, the annular space between them being filled with sawdust. One bath was kept at 25° by using an Ostwald thermoregulator, connected with a telegraphic relay, the water being heated by an incandescent lamp and well stirred. A thermometer specially calibrated for 25° was used and the temperature was constant to 0°.1. The zero bath was well filled with crushed ice and it was possible, by stirring thoroughly, to keep the temperature at 0°.1 for six or seven hours.

A sixteenth-molar solution of the violet salt was prepared by weighing the necessary quantity, which was calculated from the actual content in chromic oxide as determined by analysis, dissolving it in ice-cold conductivity water and diluting as usual at room temperature. This solution was used immediately and carried through the customary series of dilutions for conductivity measurements, readings at zero being made before those at 25°. In the same way measurements were made upon a green solution prepared from the initial violet solution by heating the latter for an hour in a pressure bottle placed in a bath of boiling water. This method of preparation of the green solution is more satisfactory than the methods used heretofore, as change of concentration by loss of solvent is avoided.

Table VII gives the results obtained in this series of measurements, and curves showing increase in conductivity with increasing dilution are plotted in Fig. VII:

Table VII.—Molecular Conductivity

$t = 0°$

Violet		Green	
V	μ	V	μ
16	85.37	16	168.1
32	100.0	32	187.7
64	117.70	64	211.2
128	139.20	128	233.2
256	166.60	256	255.2
512	194.2	512	270.8
1024	232.2	1024	282.1

Table VII—(Continued)

$t = 25°$

Violet		Green	
V	μ	V	μ
16	151.5	16	245.7
32	177.1	32	285.2
64	211.8	64	336.5
128	255.0	128	390.4
256	310.2	256	450.7
512	379.5	512	515.0
1024	476.9	1024	568.5

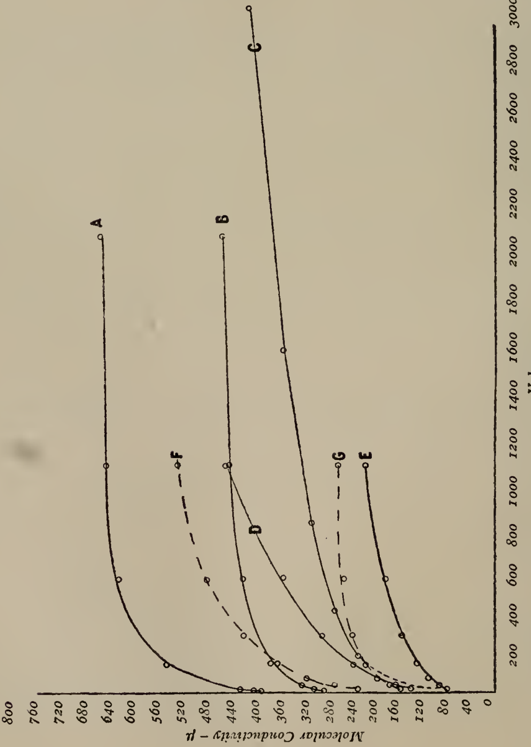

Fig. VII. A, sulphuric acid at 25°. B, sulphuric acid at 0°. C, lanthanum sulphate at 25°. D, violet solution at 25°. E, violet solution at 0°. F, green solution at 25°. G, green solution at 0°.

The curve for the green solution at 0° is of interest as it indicates a tendency to return to the violet modification at this temperature. For the sake of comparison I have plotted also results of Jones and Douglas[1] and Jones and West,[2] showing the molecular conductivity of sulphuric acid at 0° and 25°, and a curve showing the molecular conductivity at 25° of lanthanum sulphate, an unhydrolyzed salt. The points for this last curve were obtained by calculating values for molecular conductivity from the values for equivalent conductivity published by Muthmann.[3] The molar concentrations used by Muthmann are not the same as those used with the chromium sulphate, but by plotting the curve on a large scale it was possible to get the corresponding points with sufficient accuracy for comparison.

The amount of hydrolysis was calculated by the method originally proposed by Ley.[4] This is based on the difference in conductivity caused by diluting equivalent solutions of hydrolyzable and unhydrolyzable salts having a common ion. As was first shown by Ostwald,[5] normally dissociated salts show nearly constant differences in the values of the equivalent conductivity at two given dilutions. The difference between the values obtained by similarly diluting hydrolyzable salts is, of course, greater, because the total number of ions is increased by hydrolysis, and Ley proposes to take advantage of this fact for calculating the amount of hydrolysis. For this purpose he applies the formula

$$X = \frac{L - \mu_1}{\mu_2 - \mu_1}$$

where μ_1 is the conductivity of the unhydrolyzed salt, μ_2 that of the acid formed by hydrolysis, and L the conductivity measured by experiment. For each dilution, for which the degree of hydrolysis is to be calculated, it is necessary to find a value, μ_1, to represent the conductivity of the unhydrolyzed salt. This is accomplished as follows: The value μ_1 for the most concentrated solution is obtained by determining the conductivity of this solution; on the assumption that there is no hydrolysis at this concentration, $\mu_1 = L$. The values for the more dilute solutions are found by measuring the increase in conductivity caused by diluting a corresponding solution of a normally dissociated salt having the same anion and a similar constitution, and adding this increment to the initial μ_1 of the salt under investigation. Thus, assuming that there is no hydrolysis in a given salt when $V = 16$, and representing the increase in conductivity caused by diluting an analogously constituted normal salt from $V = 16$ to $V = 32$ by Δ, Ley's formula becomes:

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[1] THIS JOURNAL, **26**, 436 (1901).

[2] *Ibid.*, **34**, 415 (1905).

[3] Ber. d. chem. Ges., **31**, 1834 (1898).

[4] Z. physik. Chem., **30**, 193 (1899).

[5] Lehrbuch der allgem. Chem. (2 Aufl.). **2**, 650.

$$X_{32} = \frac{L_{32} - (\mu_{16} + \Delta)}{\mu_2 - (\mu_{16} + \Delta)}$$

In the case in hand lanthanum sulphate was used as the accessory salt, because it is constituted like chromium sulphate, but according to Muthmann is not hydrolyzed in aqueous solution. The following example shows how the amount of hydrolysis of different solutions of chromium sulphate was calculated.

The conductivity of the violet solution at 25° was found, experimentally, to be 151.5 when $V = 16$, and 177.1 when $V = 32$; the value of Δ $(V_{32} - V_{16})$ for lanthanum sulphate, taken from the curve, is 15; and the value of $\mu_2 = \mu_\infty$ for sulphuric acid at 25° is 705: therefore, $X_{32} = \dfrac{177.1 - 166.5}{705 - 166.5}$.

Table VIII.—Hydrolysis at 25°

			Percentage of hydrolysis of chromium sulphate	
V	μ for $La_2(SO_4)_3$	Δ	Violet	Green
16	139	...	...	17.02
32	154	15	1.78	22.04
64	183	44	3.19	27.68
128	220	81	4.76	33.42
256	263	124	8.08	40.74
512	304	165	16.24	51.10
1024	347	208	33.98	60.49

Table VIII gives the data used in the calculations and Fig. VIII shows the curves representing the hydrolysis of the green and violet solutions. The values for the hydrolysis, calculated by Ley's method, are less for both solutions than those obtained by Denham[1] from measurements of potential, though

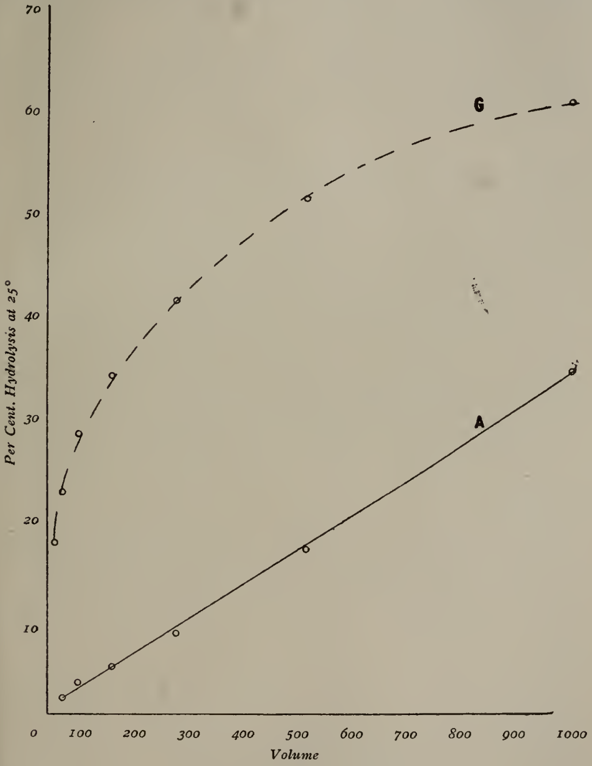

Fig. VIII. A, violet. G, green.

the ratios between values for corresponding green and violet solutions are similar to the ratios of Denham's values for the same concentration.

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[1] *Loc. cit.*

Catalytic Action as a Measure of Hydrolysis

The extent of the hydrolysis in solutions of chromic sulphate was studied in 1903 by Richards and Bonnet,[1] who acted upon the suggestion of Long[2] that the green solution of chromium sulphate, but not the violet, might be expected to cause inversion of cane sugar. They measured the speed of inversion produced by each of the solutions at approximately 17° and 30°, and estimated the amount of ionized hydrogen in the green solutions under investigation. Owing to the deep color of the solutions the polarimetric method of determining the rate of inversion could not be used, but Richards and Bonnet resorted to a method which had been developed by Kahlenberg, Davis, and Fowler.[3] This method is based upon the fact that the depression of the freezing point of water caused by invert sugar is approximately twice as great as the depression produced by the cane sugar from which the invert sugar is formed. Assuming that the catalyzing agent used for the inversion has a constant influence upon the freezing point, it is possible to follow the course of inversion by measuring, at frequent intervals, the depression of the freezing point, the point of complete inversion being reached when there is no further increase in the depression. I used the same method.

After some preliminary work at about 18° for the purpose of testing the method of procedure of Richards and Bonnet and finding, as they did, that the violet solution produced very little inversion at 18°, I decided to continue the work at a higher temperature and under somewhat different conditions.

A sugar solution was made by dissolving 250 grams of pure rock candy per liter of conductivity water. This solution was sterilized by prolonged heating in a water bath at 100°, and protected from ferments that might cause inversion by addition of a crystal of thymol, as recommended by Morse[4] in his work on osmotic pressure.

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[1] *Loc. cit.*

[2] J. Am. Chem. Soc., **19,** 683 (1897).

[3] *Ibid.*, **21,** 1 (1899).

[4] This Journal, **36,** 37 (1906).

Violet solutions of chromium sulphate of two-tenths and one-tenth molar concentration were prepared by dissolving the calculated weight of salt in cold conductivity water and from these the green solutions were obtained by heating for an hour in a pressure bottle in a bath of boiling water. The violet solutions were kept in an ice chest until needed and the green solutions were used as soon as they had been cooled to room temperature.

Equal volumes of the sugar solution and conductivity water were mixed and kept as a standard solution from which to calculate changes in depression of the freezing point. Similarly, equal volumes of the original sugar solution and a solution whose catalyzing effect was to be measured were mixed and kept in well corked test tubes which were suspended in a wire rack in a thermostat kept at approximately 30°.

In order to prevent catalytic action as much as possible the solutions were mixed in tubes immersed in ice or snow. After determining the freezing point of a mixture the tube was placed in a thermostat for a few hours, when another determination was made, this procedure being continued for several days.

The measurements of the freezing points were made with the Beckmann apparatus. The zero point of the thermometer and the freezing point of the standard sugar solution were determined at frequent intervals. In the preliminary experiments, the calculations of depression were based upon the freezing point of the sugar solution, but it seemed better in the later work to measure the depressions for all solutions directly from the freezing point of water as registered by the thermometer at the time of the experiment.

At 30° the inversion proceeded much more rapidly than at 18°, and the violet solutions were evidently hydrolyzed, a distinct change of color being noticeable as well as an increase in the depression of the freezing point.

Observations were made not only on the fresh violet and green solutions, but also on a two-tenths molar green solution which had been kept at 30° in the thermostat for two weeks, a one-tenth molar violet solution kept at room temperature for one month, a one-tenth molar green solution dehydrolyzed in an ice chest for one week, a similar solution dehydrolyzed at room temperature for fifty days, and a 0.1105 normal solution of sulphuric acid.

The results are given in Table IX. Column K gives the coefficients for the speed of inversion, calculated according to the equation

$$K = \frac{1}{t} \log_{\varepsilon} \frac{a}{a - x}$$

where a is the initial concentration of the cane sugar solution and x the amount inverted in the time t. For a may be substituted Δ, the depression of the freezing point due to cane sugar alone (0°.820), and for x the increase in the depression during time t. Transforming to ordinary logarithms and substituting, the expression becomes

$$0.4343\ K = \frac{1}{t} \log_{10} \frac{\Delta}{\Delta - (\Delta_2{}^1 - \Delta_1{}^1)}$$

Table IX.—Catalytic Action at 30°

Δ^1 = depression of freezing point of water corrected for supercooling. $\Delta_2{}^1 - \Delta_1{}^1$ = increase in depression in time t.

$$K = \frac{1}{0.4343\ t} \log_{10} \frac{\Delta}{\Delta - (\Delta_2{}^1 - \Delta_1{}^1)} \qquad (\Delta = 0°.820)$$

Violet solution. 0.2 Molar. Fresh

t (hours)	Δ^1	$\Delta_2{}^1 - \Delta_1{}^1$	K
0.0	1.332	0.0	......
16.0	1.410	0.078	0.006232
18.0	1.406	0.074	0.005257
42.5	1.607	0.275	0.009601
46.5	1.627	0.295	0.009576
69.5	1.683	0.351	0.008772
87.5	1.819	0.487	0.010300
140.0	1.977	0.645	0.011040
164.0	2.032	0.700	0.011710
			0.009061

Table IX—(Continued)

Green solution. 0.2 Molar. Fresh

t (hours)	Δ^1	$\Delta_2^1 - \Delta_1^1$	K
0.0	1.387	0.0	......
3.0	1.532	0.145	0.06463
5.0	1.577	0.190	0.05259
24.0	1.890	0.503	0.03960
28.5	1.936	0.549	0.05500
45.5	2.041	0.654	0.03510
47.5	2.036	0.649	0.03300
68.5	2.024	0.637	0.02200
92.5	2.062	0.675	0.01873
140.0	2.055	0.668	0.01217
166.0	2.073	0.686	0.01091
			0.03437

Violet solution. 0.1 Molar. Fresh

t (hours)	Δ^1	$\Delta_2^1 - \Delta_1^1$	*K*
0.0	1.094	...	....
16.5	1.146	0.052	0.003963
21.5	1.152	0.058	0.003406
39.5	1.218	0.124	0.004122
63.5	1.304	0.210	0.004659
87.5	1.368	0.274	0.004647
135.0	1.461	0.367	0.004395
148.5	1.583	0.489	0.006108
152.5	1.546	0.452	0.005255
190.0	1.630	0.536	0.005454
			0.004667

Green solution. 0.1 Molar. Fresh

t (hours)	Δ^1	$\Delta_2^1 - \Delta_1^1$	*K*
0.0	0.976	...	.....
3.0	1.005	0.029	0.01198
5.0	1.032	0.056	0.01414
23.0	1.267	0.291	0.01905
26.0	1.300	0.324	0.01933
46.5	1.434	0.458	0.01758
70.5	1.521	0.545	0.01550
99.5	1.608	0.632	0.01480
118.5	1.620	0.644	0.01298
168.5	1.664	0.688	0.01084
			0.01402

Table IX—(Continued)

Green solution. 0.2 Molar. Dehydrolyzed at 30° for 2 weeks

t (hours)	Δ^1	$\Delta_2^1 - \Delta_1^1$	K
0.0	1.373	...	.....
3.0	1.457	0.084	0.03600
23.0	1.746	0.373	0.02638
46.0	1.935	0.562	0.02514
75.0	2.058	0.685	0.02405
95.0	2.094	0.721	0.02225
142.5	2.132	0.759	0.01823
			0.02534

Violet solution. 0.1 Molar. Hydrolyzed at room temperature for 1 month

t (hours)	Δ^1	$\Delta_2^1 - \Delta_1^1$	K
0.0	1.099	...	......
25.0	1.241	0.142	0.006043
49.0	1.333	0.234	0.006857
77.5	1.480	0.381	0.008061
97.5	1.548	0.449	0.008108
145.5	1.689	0.590	0.008736
			0.007561

Green solution. 0.1 Molar. Dehydrolyzed in ice chest for 1 week

t (hours)	Δ^1	$\Delta_2^1 - \Delta_1^1$	K
0.0	0.970	...	.....
5.0	1.050	0.080	0.02053
25.5	1.257	0.287	0.01690
29.5	1.286	0.316	0.01650
48.5	1.406	0.436	0.01564
71.5	1.494	0.524	0.01425
99.0	1.570	0.600	0.01329
			0.01619

Table IX—(Continued)

Green solution. 0.1 Molar. Dehydrolyzed at room temperature for 50 days

t (hours)	Δ^1	$\Delta_2^1 - \Delta_1^1$	K
0.0	1.136	...	.....
23.0	1.415	0.279	0.01808
41.0	1.534	0.398	0.01620
69.0	1.649	0.513	0.01424
92.5	1.724	0.588	0.01365
112.0	1.782	0.646	0.01385
165.0	1.807	0.671	0.01034
187.0	1.817	0.681	0.00949
			0.01369

Sulphuric acid. 0.1105 Normal

t (hours)	Δ^1	$\Delta_2^1 - \Delta_1^1$	K
0.0	0.953	0.0	.....
2.0	1.022	0.069	0.04398
5.0	1.088	0.135	0.03596
24.0	1.381	0.428	0.03075
48.0	1.586	0.633	0.03080
53.5	1.609	0.656	0.03008
73.0	1.657	0.704	0.02679
94.0	1.687	0.734	0.02399
144.0	1.695	0.742	0.01633
169.0	1.687	0.734	0.01335
			0.02800

The inversion caused by sulphuric acid was determined for purposes of comparison. By means of similar measurements with hydrochloric acid, Richards and Bonnet estimated the number of atoms of chromium corresponding to one ion of hydrogen in the green solution.

A comparison of the coefficients for the velocity of inversion at 30° shows that the 0.2 molar violet solution catalyses nearly one-third as rapidly as the 0.1105 normal sulphuric acid solution while the corresponding green solution has a catalyzing action 1.22 times as great as the acid. According to the method of calculation of Richards and Bonnet, the green solution must contain as much ionized hydrogen as a 0.135 normal or 0.0675 molar solution of sulphuric acid. From a comparison of the relative velocities during the first part of the inversion, it is evident that the violet solution has about one-seventh the effect of the acid while the green is one and one-half times as active. The comparison of the other constants is also of interest. The two-tenths molar violet solution is nearly twice as active as the fresh one-tenth molar solution, but not much more active than the one-tenth molar solution hydrolyzed for one month at room temperature. On the other hand, the mean coefficient for the fresh one-tenth molar green solution is less than that of the same solution dehydrolyzed in the ice chest for one week and not much greater than that of the same solution dehydrolyzed at room temperature for fifty days. This is contrary to expectation but must be attributed to changes in concentration and in ionization which occur during hydrolysis and dehydrolysis. It will be seen from Table IX that the solution in question depresses the freezing point less at first than the corresponding violet solution but that the speed of inversion is greater. This cannot be due to experimental error because the work was repeated and verified. The green solution has a smaller density than the corresponding violet solution and, consequently, there is actually less of the salt present in a given volume; but the difference in concentration is too small to account for the results. Undoubtedly the number of ions in solution must also be taken into account in explaining these variations. For complete hydrolysis the ionic condition may be represented as follows:

$$[Cr_4(SO_4)_4O]SO_4 \longrightarrow [Cr_4(SO_4)O]^{++} + SO_4^{--}$$
$$H_2SO_4 \longrightarrow 2H^+ + SO_4^{--}$$

When hydrolysis is not complete there are present also the ions of chromium sulphate and therefore the total number is greater:

$$Cr_2(SO_4)_3 \longrightarrow 2Cr^{+++} + 3SO_4^{--}$$

The mean coefficients have been collected in Table X and the percentage of hydrolysis calculated according to Kahlenberg's[1] method. For the calculation, the percentage of dissociation of 0.055 normal sulphuric acid at 30° has been obtained by interpolation from curves plotted from the values of Jones and West.[1] The acid is taken as 0.055 normal and the chromium solutions as 0.1 and 0.05 molar, respectively, because of the dilution when the mixtures with the sugar solution are made. The percentages calculated must be regarded as rough approximations of the amount of hydrolysis in chromium solutions when sugar is present. They serve merely to give some idea of the relations of the violet and green solutions and of different concentrations of the same solution:

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[1] *Loc. cit.*

Table X.—Hydrolysis at 30°

Solution	K	Percentage of hydrolysis
0.2 Molar violet (fresh)	0.009061	2.21
0.2 Molar green (fresh)	0.03437	8.39
0.1 Molar violet (fresh)	0.004667	2.28
0.1 Molar green (fresh)	0.01402	6.84
0.2 Molar green (2 weeks old)	0.02534	6.18
0.1 Molar violet (1 month old)	0.007561	3.69
0.1 Molar green (1 week old)	0.01619	7.90
0.1 Molar green (50 days old)	0.01369	6.68
0.1105 Normal H_2SO_4	0.02800	

The increase in the depression with time is plotted in Fig. IX. Curves for the violet solutions indicate a steady increase in catalytic action, while those for the green solutions are similar to the curve for the acid, rising rapidly to a maximum and becoming practically horizontal. The curves for the dehydrolyzed green solutions have characteristics in common with the fresh green and fresh violet solutions of corresponding concentration, but there is greater difference between the curves of the fresh violet (0.1 molar) and the same solution kept for one month at room temperature than there is between the curves for the 0.1 molar green solution. It is evident that the change from violet to green takes place much more rapidly at room temperature than does the reverse process, as the three curves for the one-tenth molar green solution are nearly coincident.

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[1] *Loc. cit.*

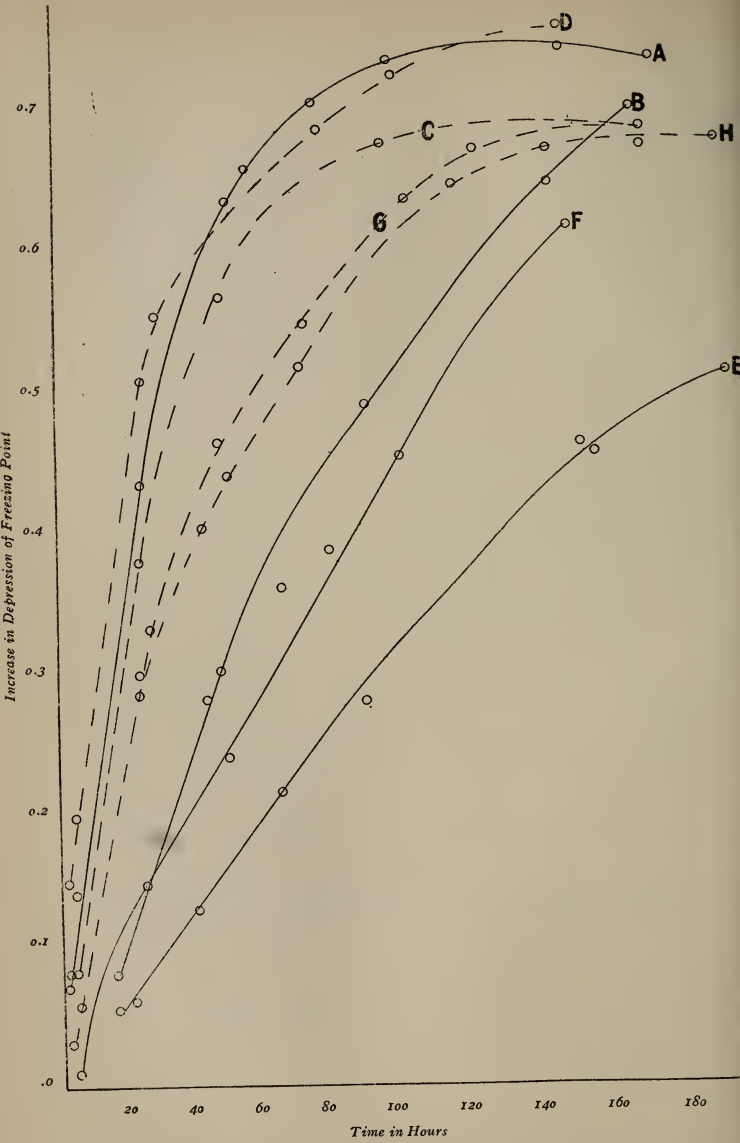

Fig. IX. Temperature, 30°. A, sulphuric acid, 0.1105 normal. B, violet solution, 0.2 molar. C, green solution, 0.2 molar (fresh). D, green solution, 0.2 molar (old). E, violet solution, 0.1 molar (fresh). F, green solution, 0.1 molar (old). G, green solution, 0.1 molar (fresh). H, green solution, 0.1 molar (old).

The experimental points for the violet solutions seem to indicate at times a condition of unstable equilibrium. This may be due to a tendency of the partially hydrolyzed solution to return to the unhydrolyzed condition at low temperatures, as fluctuations were frequently observed, causing difficulty in obtaining the true freezing points of the violet solutions. From this fact and from a comparison of the curves the conclusion may be drawn that at ordinary temperatures the green solution is more stable than the violet.

Absorption Spectra

A number of investigators have been interested in the absorption phenomena exhibited by solutions of chromium salts, including those of the sulphate. An admirable account of the literature and a bibliography of the subject are given by Jones and Anderson in their recent work, "The Absorption Spectra of Solutions."[1] An examination of this literature shows that little has been done in comparing the effects produced by violet and green solutions of the same concentration.

In comparing these solutions I have made both visual and photographic observations, using a Hilger spectroscope (mean deviation type) for visual measurements and for photographing the visible region of the spectrum, and a Fuess spectrograph, fitted with a quartz prism and quartz lenses, for work in the ultraviolet region.

The Hilger spectroscope used was similar to the instrument described by Jnnes[2] and a Nernst filament was used as a source of light. After some preliminary tests a 0.025 molar solution of the violet salt was chosen for visual observation. A small Baly tube was used, the thickness of solution being fixed at one centimeter. A marked band of absorption was observed from λ 6400 to λ 5400 with general absorption at λ 7600 and λ 4700. The bands were measured by bringing the cross-hairs in focus upon first one edge and then the other of the colored bands observed in the red and blue regions, the wave lengths being read from the drum of the instrument. The visual work was merely preliminary to the photographic observations which follow and was not extended.

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[1] Carnegie Institution of Washington: Publication No. 110 (1909).

[2] Hydrates in Aqueous Solution, p. 171. Carnegie Institute of Washington: Publication No. 60 (1907).

In using the Hilger spectroscope for photographic work the telescope was replaced by a camera. A Nernst filament was put in circuit with an ammeter and the current kept nearly constant at 0.8 ampere by means of a rheostat. A large Baly tube, provided with quartz ends and having a range of ten centimeters, was used for the solutions, the light of the Nernst filament was brought to a focus upon the slit by means of a quartz lens, and the tube of solution was then placed lengthwise between the filament and the lens. The width of slit was 0.2 mm. and the time of exposure two minutes. Sensitive panchromatic plates made by the M. A. Seed Company were used, and ten exposures made with a given solution in the tube, beginning with a thickness of ten centimeters. For purposes of reference the spectrum of hydrogen was photographed on each plate and on some plates also the spectra of mercury and helium.

The violet and green solutions used were 0.025 and 0.0125 molar. The 0.025 molar violet solution was made by weight in the usual manner, the 0.0125 molar solution was prepared from it by dilution, and the green solutions were made by heating the corresponding violet solutions in pressure bottles for an hour in a bath of boiling water—they were used immediately after preparation.

The difference in the absorption effects of the violet and green solutions is quite evident in Plates I and II. The band due to the green solution is much broader than that produced by the violet and the general absorption is greater. A comparison of Plates I and II shows the effect of dilution upon the absorbing power of the solutions.

In Plate IA the band lies between λ 6563 and λ 4861 with general absorption beginning at λ 4700. In IB the absorption for the first four exposures is general up to λ 5016 and the widest part of the band is between λ 6563 and λ 5048 with general absorption at λ 4861. In Plate II the bands are narrower, falling between λ 5900 and λ 5100 in A, and between

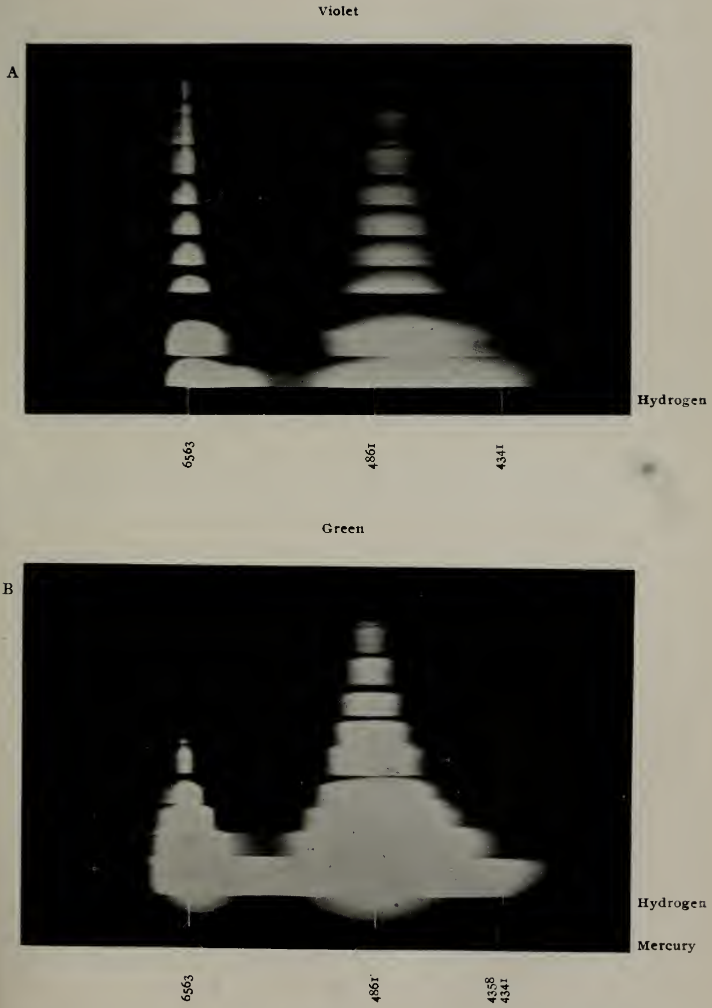
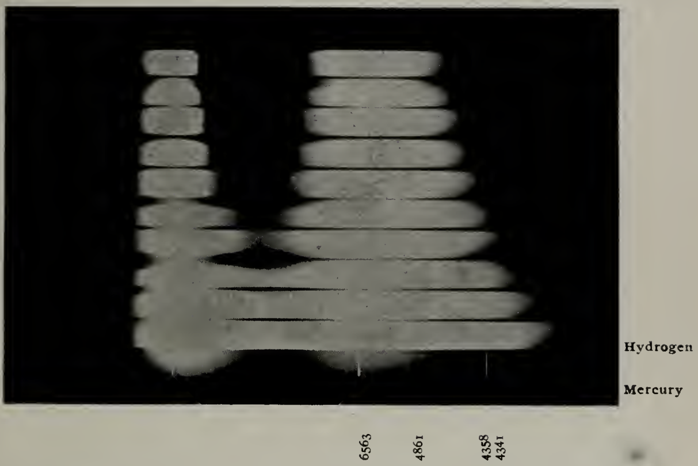


PLATE I

0.025 Molar

Violet

A



Green

B

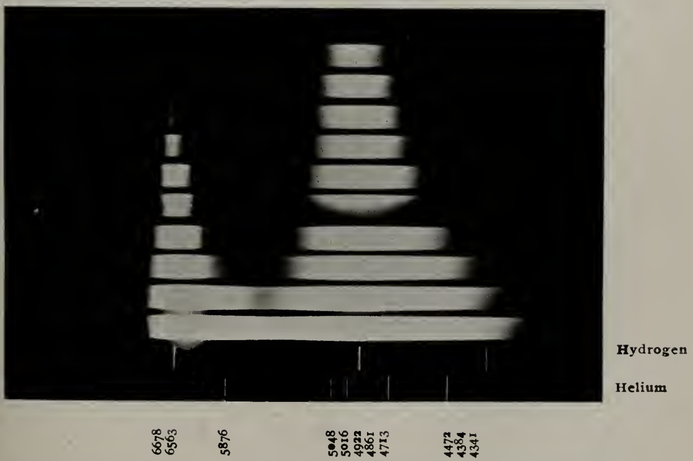


PLATE II

0.0125 Molar

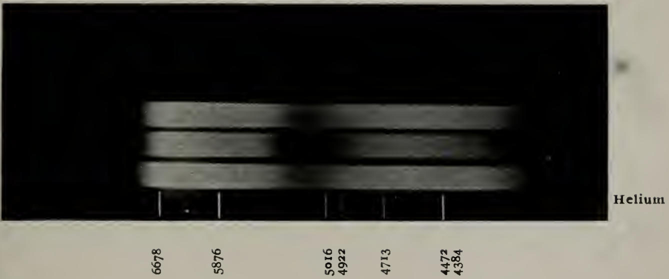


PLATE III

λ 6563 and λ 5048 in B, with general absorption at λ 4400 and λ 4600 in A and B, respectively. Plate III is given to show the effect of the sensitizing dye upon the absorption in the green.

For work in the ultraviolet a copper arc, connected with an electric light circuit, served as the source of light The large Baly tube used in the preceding work was placed between the copper arc and the quartz lens which focussed the light upon the slit of the spectrograph.

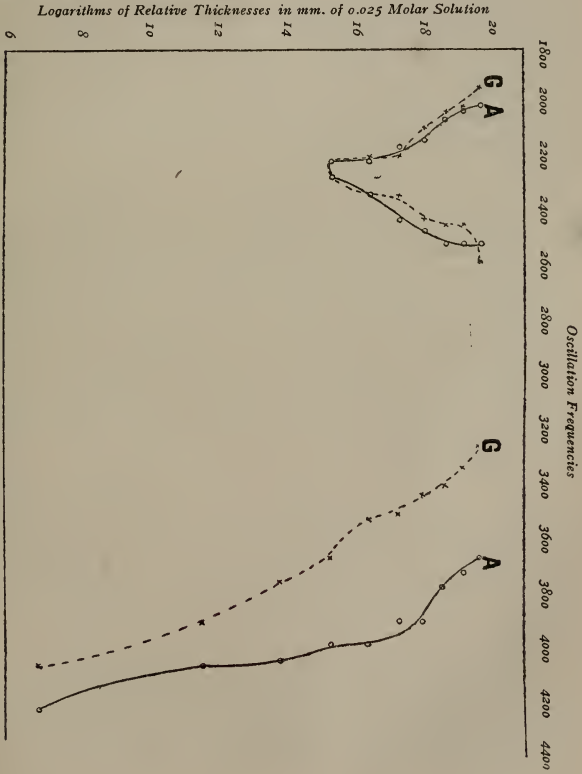


Fig. X. A, violet. G, green.

Violet and green solutions of 0.025 molar concentration were measured, the thickness being varied from ten centimeters to one. The spectrum of copper was photographed upon each plate for comparison.

A distinct band is observed in the ultraviolet region and a difference similar to that observed in the visible region is noted for the two solutions.

From measurements of the lines in the spectrum of copper the absorption bands for the two solutions were determined, the results being plotted in Fig. X, where the oscillation frequencies are abscissas, and logarithms of the thickness of solution are the ordinates. From these curves it appears that the greater difference between the two solutions is in the region of general absorption, the other boundary of this band being shown in Plate I.

SUMMARY

The results of this research may be summarized as follows:

1. The yield of violet chromic sulphate from chromic acid is increased by carrying out the reduction at low temperatures, by allowing considerable time for deposition of the salt, and by keeping all solutions as cold as possible during the processes of purification.

2. Solutions of the violet salt are not stable at room temperature and the results of any measurements are more reliable if the solutions are kept at a low temperature until needed for the experiments.

3. Measurements of density, viscosity and electrical conductivity indicate that a gradual change occurs as the violet solution becomes green with increasing temperature, and that the reverse change with falling temperature is also a gradual one. The same conclusion holds with reference to the changes that occur in the two solutions when the concentrations are varied.

Assuming that the change in color is due to hydrolysis, the conclusion to be drawn, from the changes in density, viscosity and conductivity, is that for each temperature and each concentration there is a condition of equilibrium between the violet and green modifications.

4. The hydrolysis, as determined by measurements of conductivity, is evidently increased in both solutions by dilution. Measurements of the conductivity of the violet solution at zero indicate a small amount of hydrolysis which becomes measurable with increasing dilution, and a tendency of the green solution to become dehydrolyzed at the low temperature.

5. By comparing the catalytic effect produced by the chromium solutions with that due to a standard solution of sulphuric acid the hydrogen ion concentration of a given solution can be estimated and from this the percentage of hydrolysis can be roughly calculated.

Catalytic measurements with corresponding solutions of different ages indicate that the change from violet to green is much more rapid than the reverse process.

6. Observations of the absorption effects caused by the solutions indicate that the change in color in chromium sulphate solutions is not due to simple hydrolysis, but is the result of a process that involves both hydrolysis and change in structure.

7. All of the measurements and the calculations of hydrolysis lead to the conclusion that the reaction to which the change of color is due does not take place in successive steps involving the formation of a number of intermediate compounds, but that it is a single process tending to an equilibrium defined by the variables time, temperature and concentration.

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June, 1912

A CHRONOLOGICAL BIBLIOGRAPHY OF THE CHANGE FROM VIOLET TO GREEN IN CHROMIUM SULPHATE

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1908. Colson, Albert. Bull. soc. chim., [4] 3, 90.
1908. Denham, H. G. Elektrometrische Bestimmung der Hydrolyse des blauen und grünen Chromisulfates. Z. anorg. Chem., 57, 361.
1908. Wyrouboff, H. G. Sur la théorie de la valence et la constitution des sels. Ann. chim. phys., [8] 13, 523.

REVIEWS

TECHNICAL METHODS OF CHEMICAL ANALYSIS. Edited by GEORGE LUNGE, PH.D., DR. ING., Emeritus Professor of Technical Chemistry, Federal Polytechnic School, Zurich. English translation from the latest German edition, adapted to English conditions of manufacture. Edited by CHARLES ALEXANDER KEANE, D.Sc., PH.D., Principal and Head of the Chemical Department, The Sir John Cass Technical Institute, London. Volume II, Part I, xxvii + 610 pp., and Part II, xii + 641 pp. New York: D. Van Nostrand Company. 1911. $12.00.

To review adequately a volume of such enormous size, of so many subjects, and involving so much detail would require much more space than is ordinarily granted to such a review. Indeed, it is doubtful whether it would be profitable unless the reviewer were to associate with him as many readers expert in their line as the German and English editors have associated with them. That such a work should be successful necessarily involves the association of a large number of experts in special fields. The names of both the German and English subeditors is evidence of the good intentions of the publishers. The list of the subjects treated is not large, considering the size of the two parts constituting the volume. Iron, including ores, iron and steel analysis, metals other than iron, and metallic salts, artificial manures, feeding stuffs, explosives, matches and fireworks, calcium carbide and acetylene, illuminating gas and ammonia, coal tar, and organic dyes are the subjects treated. These subjects alone do not adequately represent the contents. For instance, under the title, "Metals Other than Iron," are given methods of analysis, in nearly all cases including the latest information, of all the ores and the technically useful metals. The number of pages devoted to this chapter is 284. To organic dyes is given 341 pages.

To anyone doing general work and not having available a first-class working library this book would be invaluable.

H. F.

A DICTIONARY OF APPLIED CHEMISTRY. By SIR EDWARD THORPE, C.B., LL.D., F.R.S., Professor of General Chemistry and Director of the Chemical Laboratories of the Imperial College of Science and Technology, South Kensington, London, assisted by Eminent Contributors. In Five Volumes. Revised and Enlarged Edition, with Illustrations. Vol. I, A-Che. London, New York, Bombay and Calcutta: Longmans, Green & Co. 1912. pp. viii + 758. Price, $13.50.

That a new and modernized edition of this well known work will soon be ready is welcome news to all chemists and engineers having to deal with industrial chemical problems. The original edition of 1890–1893 found a place in nearly every library and works' laboratory and few books of reference have had such frequent use. The concise and handy form in which the information is presented won for the book a high place in the regard of all manufacturing chemists. Every new question in the factory procedure would send the chemist and engineer to the "Dictionary" for information concerning the matter. But in the twenty odd years since the original issue, many new substances which have become common articles of commerce, such as the important and interesting electric furnace products, and processes which are now firmly established industrially, could not be found in the "Dictionary," while information relating to many other subjects was meager or entirely out of date. It is, therefore, a matter of satisfaction to find such complete treatment of abrasives, including carborundum and alundum, of acetylene as an illuminant, of argon, of anaesthetics, of boiler incrustations and deposits, of bronze powders, of chemical affinity, including equilibrium, catalysis, etc., of casein, of synthetic camphor, of Taylor's electric furnace process for carbon disulphide, and numerous other substances. Moreover, a large amount of new material has been introduced into the old articles, so that the final effect has been the practical rewriting of nearly the entire book. Also many new illustrations are introduced. Perhaps the largest amount of new material added occurs in the article on "Analysis" which has been increased from 56 to 101 pages, of which 16 pages are devoted to the new field of Electrochemical Analysis, including many illustrations of the various appliances devised by Classen, E. F. Smith, F. M. Perkin, Frary, Gooch, and others.

Copious references to the more recent work of chemical investigatiors brings the data up to about the end of 1910, and much of the older out-of-date matter has been eliminated. Although most of the articles are by British authors, considerable attention is devoted to American practice and many references to American journals and publications increase the value of the work to users in this country.

The general plan of the original publication has been retained in this edition: the arrangement of subjects is alphabetical, with cross references in all cases which may be classed under different heads. Notwithstanding collaboration of so many authors, there is general uniformity in nomenclature, abbreviations, references, weights, etc., evidencing much care here also on the part of the editor.

The make-up of the book is vey satisfactory, with clear print on heavy paper, and strong cloth binding suitable for the hard usage which reference books must endure. The proof-reading has been very carefully done and this new issue will at once meet favor as a standard reference work. F. H. THORP

DIE CHEMIE DER CELLULOSE, unter besonderer Berücksichtigung der Textil- und Zellstoffindustrien. VON DR. PHIL. CARL G. SCHWALBE, a.o. Professor an der Grossh. Techn. Hochschule zu Darmstadt. Zweite Hälfte (Schluss des Werkes). Berlin: Verlag von Gebrüder Borntraeger. 1911. pp. xii + 273–665. Price, M. 14.80.

In the first 90 pages of this half the discussion of cotton cellulose is continued from the previous half, its esters, nitrates, acetates, viscose, etc., as well as its decomposition products and consitution, being taken up.

From this point on the subject matter is more varied, including information relating to the compound celluloses, the technical preparation of raw materials, the celluloses separated from the raw materials, etc. There is also a short section devoted to the mercerization of cotton, artificial silk manufacture, the treatment of rags for paper stock and the preparation of parchments and vulcanized fiber. The final section is devoted to the analytical methods, both qualitative and quantitative, which are used in cellulose chemistry.

The book closes with an introduction and table of contents and an alphabetical index, both by authors and subjects, covering both parts. The arrangement of the work is, in general, excellent and the indexes are good, especially that of authors' names. The subject index could have been rather more detailed to good advantage but when used in conjunction with the contents little trouble is encountered in locating any desired statements. The typography is pleasing and but few errors are observed, among those noted being two on p. 518 where the yield on the absolutely dry basis is given as 24 per cent. for *P. alba*, while for the figures given it should be 35 per cent. Toward the bottom of the page the scientific name of hemlock is given as *Tanga canadensis* while it should be *Tsuga canadensis*.

This volume presents the chemistry of cellulose up to the date of its publication and covers the ground with remarkable thoroughness. The care which the author has used in reviewing the literature of the subject is evidenced by the presence of over fourteen hundred references to original articles in this half.

There are of course statements in this book to which some will take exceptions, but in the reviewer's opinion it is by far the best work on the subject and should be in the hands of all who are interested in any way in the chemistry or technics of cellulose. E. SUTERMEISTER

THE CHEMISTRY OF BREAD-MAKING. By JAMES GRANT, M.SC. TECH., F.I.C., F.C.S., Head of the Fermentation Industries Department in the Municipal School of Technology, Manchester; Examiner in Chemical Technology in the Victoria University, Manchester. With plates. New York: Longmans, Green & Co. London: Edward Arnold. 1912. pp. vii + 224. Price, $1.40.

The author states in the preface that this book "is put forward in the hope that it may fill a gap which undoubtedly exists in the literature and text-books on this subject." Its contents, however, show a surprising lack of familiarity with recent excellent contributions to the literature on the chemistry of wheat and its products, particularly those which have been published in this country. Apparently the writer is ignorant of the large mass of material which has been presented in the bulletins and reports of the Agricultural Experiment Stations, during the past ten years.

The first 100 pages of the book are devoted to a review of some of the elements of physics and chemistry, and the next 50 pages to the mechanics and biology of milling and baking. It is the author's recommendation that these be studied "in conjunction with some simple text-books on chemistry, physics, mechanics, and the elements of biology and botany." It is the reviewer's opinion that the chapters on these subjects add little to the material which would be found in such text-books and that the questionable application of some of the matter here presented to the field of bread-making will tend to confuse rather than clarify the situation, in the minds of readers unfamiliar with these sciences.

The book contains many statements which, in the light of the positive results of recent researches, must be considered as inaccuracies. These are particularly noticeable in the discussions of the distribution of starch and proteid matter in the wheat berry, of the nature and functions of glutenin and gliadin and of the nature of color and other properties of flour. The chapter on the "Organic Constituents of Cereals" contains rather elaborate descriptions and formulas for various hydroxy acids, an excellent summary of the composition of fats, with formulas and reactions for saponification, but a very incomplete discussion of the proteids; giving properties and structure only of asparagine, a compound not found in ordinary cereals.

The plates which are reproductions of photographs of portions of the wheat, flour and berry are excellent, but the diagrams intended to represent different parts of the wheat plant are very poor. The sketch of wheat berries, on page 97, would scarcely be recognized as such by anyone who has ever seen wheat grains, and certainly would convey a very inadequate impression to one who has not.

The book abounds in English terms which are unfamiliar, if not unintelligible, to an American reader. In general, it may be said that, while the purpose of the writer in preparing the book is highly commendable, the book itself is hardly to be regarded as a valuable contribution to the literature of the subject, at least for American readers. R. W. THATCHER

AN EXPERIMENTAL COURSE OF PHYSICAL CHEMISTRY. Part II. Dynamical Experiments. By JAMES FREDERICK SPENCER, D.Sc. (Liverpool), PH.D. (Breslau), Assistant Lecturer of Chemistry, Bedford College (University of London), Fellow of Victoria University. London: G. Bell and Sons, Ltd. 1911. pp. xvi + 256. Price, 3 s. 6 d.

The appearance of Volume I of this book has already been noticed in THIS JOURNAL.[1] Says the author: "Owing to the large number of chemical students who are insufficiently grounded in physics, it has been deemed well to describe, in detail, methods of measuring the electrical quantities, resistance, capacity, electromotive force and dielectric constant in the chapters where the physical chemical relationships of those properties are discussed." This is certainly a wise mode of procedure.

The choice of experiments throughout this volume is excellent, and the descriptions for the most part adequate and satisfactory.

About the only adverse criticism is that a love for the antique still manifests itself, especially in the migration velocity apparatus on page 81, which has been superceded by far better forms. H. C. J.

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[1] Vol. **46**, p. 649.

Die Methoden der Massanalyse. Zugleich 8. völlig umgearbeitete Auflage von Fr. Mohr's Lehrbuch der chemisch-analytischen Titriermethode. Von Dr. H. Beckurts, Geh. Medizinalrat, o Professor und Vorstand des pharmaz.-chemischen Instituts der Technischen Hochschule Braunschweig, unter Mitwirkung von Dr. O. Lüning. Zweite Abteilung. Mit 111 eingedruckten Abbildungen. Braunschweig: Druck und Verlag von Friedr. Vieweg und Sohn. 1912. pp. v + 360. Price, M. 10.

The nature of this extensive work on Volumetric Analysis was discussed in the review of Part I.[1] Part II deals with oxidation and reduction processes, with a critical review of the literature and descriptions of the more generally accepted methods. It includes the determination of a number of the rarer elements, as cerium, lanthanum, didymium, niobium, etc., as well as a large number of organic analyses of different kinds. The numerous references cover the literature through 1910. The final volume (Part III) is in press and will complete a work that should be of great value to the analyst, not only as an index to the literature but also as a source of concise information with regard to special analyses. R. S. Williams

E. Merck's Annual Report of Recent Advances in Pharmaceutical Chemistry and Therapeutics. 1910, Volume XXIV. Darmstadt: E. Merck. 1911. pp. 419.

Of the present volume of the "Annual Report," 38 pages are given to the "Cacodylates and their Therapeutic Uses," and 25 pages to Kephir, then follows the usual report on Preparations and Drugs. Especially interesting at this time is the section on Salvarsan, with its 250 or so references to the literature. C. A. R.

Prüfung der chemischen Reagentien auf Reinheit. Von E. Merck. Zweite Auflage. Darmstadt: E. Merck. 1912. pp. v + 332.

Few changes have been made in the second edition of this very useful book, except that new reagents which have come into use since the appearance of the first edition in 1905, such as benzidine, dimethylglyoxime, nitron, have been included, together with references to the literature bearing on them.

C. A. R.

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[1] This Journal, **45**, 89 (1911).

VOL. XLVIII SEPTEMBER, 1912 NO. 3

AMERICAN

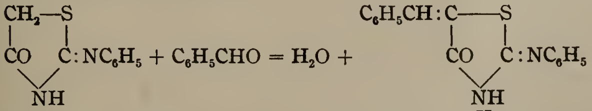
CHEMICAL JOURNAL

[Contributions from the Sheffield Laboratory of Yale University]

CCI.—DESMOTROPISM IN THE PSEUDOTHIOHYDANTOINS

BY TREAT B. JOHNSON AND JOSEPH A. AMBLER

It is known that certain pseudothiohydantoins, which contain the thioglycollide grouping —S.CH_2.CO—, behave in a tautomeric manner with respect to their reactions with aldehydes and acetic anhydride. For example, the methylene hydrogens in the stable arylhydantoins (I), and also those of the disubstituted pseudothiohydantoins, (III) and (IV), are capable of reacting with aldehydes in a manner similar to that of benzyl cyanide,[1] forming condensation products corresponding to the hydantoin[2] (II).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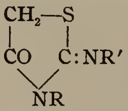
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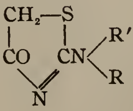
IV

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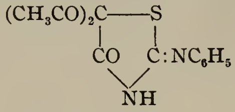
[1] Meyer: Ann. Chem. (Liebig), **250**, 124.
[2] Wheeler and Jamieson: J. Am. Chem. Soc., **25**, 366.

On the other hand, the stable hydantoins (I) react smoothly with acetic anhydride, forming stable diacetyl derivatives.[1] No definite constitution, however, was assigned to these diacetyl compounds, but it was shown that they do not behave as acetoacetic acid derivatives. In other words, the hydrogens of the methylene group (CH_2) are not directly replaced by both acetyl groups as represented in formula (V) or by one acetyl radical as represented in the two hydantoins (VI) and (VII). This was established by the fact that these diacetyl derivatives are insoluble in alkali. Formula (VIII) is not to be considered since it represents an unstable structure—an imido acid anhydride,[2] which would be expected to rearrange into its stable isomer (VI).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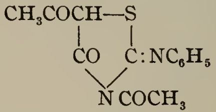
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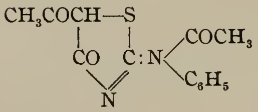
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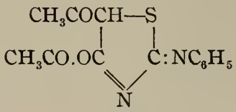
VIII

It follows, therefore, from these results that the structure of these pseudothiohydantoins (I) cannot be established by acetylation or by their behavior towards aldehydes. In other words, the chemical evidence does not enable us to conclude whether the pseudothiohydantoin nucleus is to be assigned a definite constitution or whether its twofold character is due to the fact that we are dealing with a case of dynamic isomerism. The chief object of the work described in this paper was to obtain evidence, if possible, from observations of optical activity, which would serve to indicate that a pseudothiohydantoin is capable of undergoing a dynamic change in an aqueous solution. We shall describe some interesting results which we have obtained by examination of the rotation of an active salt of pseudothiohydantoinacetic acid.

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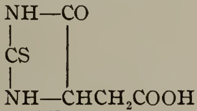
[1] Wheeler and Johnson: This Journal, **28**, 121.

[2] Wheeler and Johnson: *Ibid.*, **30**, 24.

If one considers only carbon substitution products and disregards also tautomeric and imido acid anhydride modifications theoretically possible, there are two thiohydantoinacetic acids, viz., the normal acid, thiohydantoin-4-acetic acid (IX), and the pseudo acid, pseudothiohydantoinacetic acid (X), which we used in our work. Of these two acids this pseudo form (X) is the only one which has hitherto been described in the literature. It was first prepared by Tambach[1] by the action of thiourea on bromosuccinic acid. It was later synthesized by Andreasch[2] by the addition of thiourea to maleic or fumaric acids, by the action of cyanoamide on thioaspartic acid, and also by the reduction of dehydrothiohydantoinacetic acid (XI) with sodium amalgam.[3] A description of the unknown acid (IX) has been given in a recent publication from this laboratory.[4]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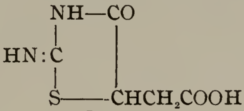
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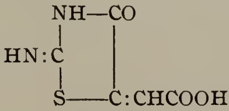
XI

Regarding the constitution of pseudothiohydantoinacetic acid Andreasch[5] writes as follows: "Die Thiohydantoinessigsäure enthält übrigens ein asymmetrisches Kohlenstoffatom und kann daher in ihren optischen Isomeren existieren; auf eine eventuelle optische Activität wurde nicht geprüft." So far as the writer is aware, Andreasch made no attempts later to obtain the active modifications of this acid. We now find that this acid combines with the active base brucine, forming a stable salt which is extremely soluble in water. It was easily purified by crystallization from 95 per cent. alcohol. We have subjected this salt to a systematic fractional crystallization and made a very thorough study of its rotatory power in aqueous solution. All attempts, however, to separate two optical modifications of the salt were without success. The salt was found to have a definite specific rotation, in aqueous solution, of $[\alpha]_D^{20}$ —12°.65. We obtained no evidence of the existence of the other active modification. Furthermore, when this active salt, $[\alpha]_D^{20}$ —12°.65, was decomposed by hydrochloric acid, the original inactive pseudothiohydantoinacetic acid, melting at 245–250°, was obtained. These results therefore indicate that pseudothiohydantoinacetic acid does not contain a true asymmetric carbon atom.

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[1] Ann. Chem. (Liebig), **280**, 233 (1894).

[2] Monats., **16**, 789.

[3] *Ibid.*, **18**, 78.

[4] Johnson and Guest: This Journal, **48**, 103.

[5] *Loc. cit.*

We have now made the interesting observation that a solution of the brucine salt in water does not retain its original activity, while a crystalline specimen showed no change in activity. In other words, the salt exhibits mutarotation in this solvent. In fact, the specific rotation $[\alpha]_D^{20}$ —12°.65 given above is the average of a series of measurements, which were made immediately after dissolving the salt in water. If the aqueous solution is allowed to stand at ordinary temperature the rotatory power begins to increase slowly and finally attains a constant maximum value of $[\alpha]_D^{20}$ —25°.0–25°.2. The rapidity with which this transformation takes place increases in marked degree with the rise in temperature. At the ordinary laboratory temperature of 20°–25° the change was complete after 72 hours, but on heating the solution to boiling the transformation is completed within a few minutes. It is an interesting fact that the relation of the initial to the final rotation is 2 : 1.

The cause of this interesting change is very probably to be found in the transformation of desmotropic modifications of the hydantoinacetic acid. Whether we are dealing here with a case of keto-enol desmotropy analogous to that observed by Dakin[1] in the case of the active hydantoins, or whether it involves a change in the amidine linking of the hydantoin nucleus, must be decided by further work. These variations shown in specific rotation, however, do not depend on the phenomenon of hydrolytic dissociation because the specific rotation was always the same, $[\alpha]_{D}^{20}$ —12°.6 and $[\alpha]_{D}^{20}$ —25°.0, when the rotation was determined in solutions of different concentrations. By increasing the dilution, the number of active aggregations should be increased if the salt underwent hydrolysis, and, consequently, the specific rotation should be different for each concentration and the greatest in dilute solutions.

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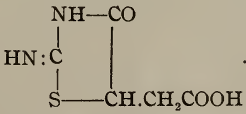
[1] THIS JOURNAL, **44**, 48.

SUMMARY

The brucine salt of pseudothiohydantoinacetic acid is capable of undergoing a change in an aqueous solution, and this can be followed quantitatively by means of the polarimeter.

The variations in specific rotation are not due to the phenomenon of hydrolytic dissociation, but are probably in response to a desmotropic change in the pseudothiohydantion nucleus of the salt.

EXPERIMENTAL PART

Pseudothiohydantoinacetic Acid, 

$$\begin{array}{ll} & \mathrm{NH-CO} \\ \mathrm{HN{:}C} & \;|\qquad\;| \\ & \mathrm{S{-}{-}CH.CH_2COOH} \end{array}$$

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Andreasch[1] prepared this hydantoin by heating fumaric or maleic acid and an equivalent amount of thiourea with water in a closed vessel at 105°, and states that it decomposes at 210–212° without melting. He qualifies this, however, as follows: "doch scheint die Schnelligkeit des Erhitzens für den Zersetzungspunkt maassgebend zu sein, da mitunter auch ein höherer Zersetzungspunkt (218°) beobachtet wurde." Tambach[1] likewise gives the decomposition point as 210°. We prepared the acid in the following manner: Five grams of fumaric acid and 3.3 grams of thiourea were ground together and the powder suspended in 4 cc. of water. This was then heated, in a small flask, on a boiling water bath for two days. The solid did not dissolve at any period of the reaction. After the reaction was complete the hydantoin was purified by crystallization from boiling water. It separated on cooling in beautiful, prismatic crystals, which decomposed from 245°–250° with effervescence. There was no evidence of melting at 210°. Moreover, we prepared the acid by Tambach's method and obtained the same acid melting at 245°–250°. If the sulphuric acid bath is heated rapidly the decomposition point can be raised as high as 260°. The yield of purified acid was 6 grams, or 72 per cent. of the theoretical. The isomeric thiohydantoinacetic acid[1] melts at 222° with effervescence. Nitrogen determinations (Kjeldahl):

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[1] *Loc. cit.*

	Calculated for $C_5H_6O_3N_2S$	Found I	Found II	Found III	Found IV
N	16.09	15.8	15.8	15.63	15.87

Hydrochloride, $C_5H_6O_3N_2S.HCl$.—Pseudothiohydantoinacetic acid possesses weak basic properties. The double platinum chloride salt has been made by Tambach, but it undergoes decomposition in water, giving the original hydantoin. We succeeded in isolating the hydrochloride in the following manner: A small amount of the hydantoin was dissolved in 10 cc. of boiling hydrochloric acid and the solution cooled and allowed to stand. The hydrochloride deposited in the form of prisms arranged in radiating groups. These were filtered off and dried in a desiccator over potassium hydroxide. The salt melts at 210°–212° with effervescence and is dissociated by cold water into hydrochloric acid and the hydantoin melting at 245°–250°. Analysis (Kjeldahl):

	Calculated for $C_5H_6O_3N_2S.HCl$	Found
N	13.33	13.09

Hydrolysis of the Pseudothiohydantoinacetic Acid.—One gram of the hydantoin acid, melting at 245°–250°, was boiled with 20 cc. of hydrochloric acid for two hours. The solution was then concentrated and cooled, when prisms separated. They were filtered off and purified by recrystallization from hot water. The compound melted at 169°–170° and was identified as dioxythiazoleacetic acid.[1]

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[1] Johnson and Guest: *Loc. cit.*

Sodium Salt, $C_5H_5O_3N_2SNa.3H_2O$.[2]—This salt was obtained from our acid melting at 245°–250°; 0.5019 gram of the acid was dissolved in 36.3 cc. of a 0.1 N sodium hydroxide solution and this then concentrated on the steam bath. On cooling, the sodium salt was obtained in the form of large, flat, tabular crystals.

Water determination:

I. 0.4674 gram salt lost at 100°–110° 0.1031 gram H_2O.

	Calculated for $C_5H_5O_3N_2SNa.3H_2O$	Found
H_2O	21.60	22.0

Barium Salt, $(C_5H_5O_3N_2S)_2Ba.H_2O$.—One gram of our pseudothiohydantoinacetic acid was dissolved in 72.3 cc. of 0.1 N sodium hydroxide solution and this solution then concentrated to a volume of about 10–15 cc. The required amount of barium chloride, $BaCl_2.2H_2O$ (0.7012 gram), dissolved in water, was added to this solution. The resulting mixture was heated to boiling, filtered from a trace of barium carbonate and the solution concentrated and cooled. The barium salt then separated. This was dried, for analysis, in the air.

Water determination: Loss at 110°–120°.

I. 0.8110 gram substance lost 0.0317 gram of H_2O.

Barium determination:

II. 0.7793 gram substance gave 0.3076 gram $BaCO_3$.

	Calculated for $(C_5H_5O_3N_2S)_2Ba.H_2O$	Found I	Found II
H_2O	3.59	3.91	...
Ba	28.40	..	28.35

Active Brucine Salt, $C_5H_6O_3N_2S.C_{23}H_{26}O_4N_2$.—This salt was prepared by suspending 15 grams of the hydantoinacetic acid and 33.95 grams of Kahlbaum's brucine in water and then warming until a clear solution was obtained. The acid and base are practically insoluble in water while the salt is extremely soluble. The aqueous solution was evaporated to dryness and the crude salt then purified by crystallization from 95 per cent. alcohol. It separated from this solvent in blocks which melted at 177° with effervescence. It was dried for analysis at 100°.

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[1] Andreasch and Tambach: *Loc. cit.*

[2] Tambach: *Loc. cit.*

Nitrogen determination (Dumas method):

I. 0.1043 gram substance gave 8.6 cc. of N_2 at 18° and 765 mm. pressure.

	Calculated for $C_5H_6O_3N_2S.C_{23}H_{26}O_4N_2$	Found
N	9.8	9.58

The cinchonine and strychnine salts of pseudothiohydantoinacetic acid are extremely soluble in cold water.

Optical Rotation.—Attempts to resolve the acid into optical isomers by fractional crystallization of the brucine salt were without success. The specific rotation, in aqueous solution, was $[\alpha]_D^{20}$ —12.65° and after a systematic crystallization of the salt from 95 per cent. alcohol we obtained no evidence of any other optical modification. When this active salt was decomposed by cold hydrochloric acid the original acid was obtained and was optically inactive. For example: some of the pure salt, having an initial specific rotation of $[\alpha]_D^{20}$ —12°.6, was dissolved in the least possible amount of water and hydrochloric acid added drop by drop until the hydantoinacetic acid deposited. The solution was then warmed gently to dissolve the brucine hydrochloride and the acid recrystallized from water to separate all traces of the brucine salt. The acid melted at 245°–250° as before; 0.3568 gram of it was then dissolved in cold concentrated hydrochloric acid (25 cc.) and the solution diluted to 50 cc. with water. This showed no optical activity even after long standing.

In order to determine whether the salt exhibits mutarotation, which would serve to indicate a tendency to undergo change into desmotropic modifications, its rotatory power in water solution was determined immediately after solution and also after the solutions had stood for different periods. The results obtained are given in Table I.

Table I.

Rotatory power in water solution. $c = 5$, $l = 1$, temperature = 20°

Crop A

	$[\alpha]_D^{20}$
Rotation after 2–3 hours	—15°.74
Rotation after 72 hours	—24°.8
Rotation after 216 hours	—24°.8
Rotation after 336 hours	—25°.0

Crop B

Immediate rotation	—12°.76
Rotation after 72 hours	—24°.6
Rotation after 168 hours	—25°.2
Rotation after 264 hours	—24°.8
Rotation after 346 hours	—25°.0

Crop C

Immediate rotation	—13°.04
Rotation after 72 hours	—25°.0
Rotation after 144 hours	—25°.0
Rotation after 240 hours	—25°.0

Crop D

Immediate rotation	—11°.9–12°.0
Rotation after 72 hours	—25°.0
Rotation after 144 hours	—25°.0
Rotation after 240 hours	—25°.0

The effect of heat on the rotatory power is shown by inspection of the results given in Table II.

Table II

Rotation in aqueous solution after heating to boiling and cooling.

$c = 5$, $l = 1$, temp. = 20°	$[\alpha]_D^{20}$ —25°.2
$c = 7$, $l = 1$, temp. = 20°	$[\alpha]_D^{20}$ —25°.2

New Haven, Conn.
June 1, 1912

THE REACTION BETWEEN ORGANIC MAGNESIUM COMPOUNDS AND CINNAMYLIDENE ESTERS

IV. REACTIONS WITH METHYL α-METHYLCINNAMYLIDENACETATE

By Marie Reimer and Grace Potter Reynolds

The object of the series of investigations, of which the work described in this paper forms a part, was to study the effect of a second ethylene linkage on the reactivity of the system C : C.C : O. For this purpose the reaction chosen was that between the Grignard reagent and esters of cinnamylidenacetic acid and its α-substitution products.

In the present paper the results obtained with methyl α-methylcinnamylidenacetate are described.

With phenylmagnesium bromide the reaction consists in a replacement of the alkoxyl group of the ester by the phenyl group and addition, in the 1,4 position, of a second molecule of phenylmagnesium bromide according to the following equations:

$$C_6H_5CH : CHCH : C(CH_3)COOR + C_6H_5MgBr \longrightarrow C_6H_5CH : CHCH : C(CH_3)COC_6H_5 + MgBrOR$$

$$C_6H_5CH : CHCH : C(CH_3)COC_6H_5 + C_6H_5MgBr \longrightarrow C_6H_5CH : CHCH(C_6H_5)C(CH_3) : C(C_6H_5)OMgBr$$

$$C_6H_5CH : CHCH(C_6H_5)C(CH_3) : C(C_6H_5)OMgBr + H_2O \longrightarrow C_6H_5CH : CHCH(C_6H_5)CH(CH_3)COC_6H_5$$

Two isomeric ketones, melting at 112° and 85°, respectively, are formed in this reaction. These ketones contain an ethylene linkage as well as two unequal asymmetric carbon atoms. If the isomerism were geometric, oxidation of the two ketones at the ethylene linkage should give rise to the same ketonic acid. It has been found, however, that the ketones give, on oxidation, isomeric ketonic acids. They are, therefore, racemic compounds.

The high-melting ketone reacts with phenylmagnesium bromide in the cold to give a quantitative yield of tertiary alcohol. The low-melting ketone, on the other hand, does not react with this reagent even on long boiling in ether solution. Its configuration, therefore, is such as to prevent the reaction with phenylmagnesium bromide. Although the ketones are undoubtedly optical isomers, their configuration must, then, be to a certain extent fixed, either as in the case of the symmetrically disubstituted succinic acids[1] or as a result of restricted rotation at the ethylene linkage.

With benzylmagnesium bromide the first reaction consists in replacement of the alkoxyl group of the methyl α-methylcinnamylidenacetate by the benzyl group; from this intermediate ketone two products are formed, one a ketone by addition of benzylmagnesium bromide in the 1,4 position, the other a tertiary alcohol by addition of the reagent in the 1,2 position. From this alcohol a hydrocarbon results by spontaneous loss of one molecule of water:

$$\begin{aligned}&C_6H_5CH : CHCH : C(CH_3)COOR + C_6H_5CH_2MgBr \longrightarrow \\ &\qquad C_6H_5CH : CHCH : C(CH_3)COCH_2C_6H_5 + MgBrOR\end{aligned}$$

$$\begin{aligned}&C_6H_5CH : CHCH : C(CH_3)COCH_2C_6H_5 + C_6H_5CH_2MgBr \longrightarrow \\ &\qquad C_6H_5CH : CHCH(CH_2C_6H_5)CH(CH_3)COCH_2C_6H_5\end{aligned}$$

$$\begin{aligned}&C_6H_5CH : CHCH : C(CH_3)COCH_2C_6H_5 + C_6H_5CH_2MgBr \longrightarrow \\ &\qquad C_6H_5CH : CHCH : C(CH_3)C(CH_2C_6H_5)_2OH \longrightarrow \\ &\qquad C_6H_5CH : CHCH : C(CH_3)C(CH_2C_6H_5) : CHC_6H_5 + H_2O\end{aligned}$$

With ethylmagnesium bromide the only primary product isolated was a tertiary alcohol formed in accordance with the following equation:

$$\begin{aligned}&C_6H_5CH : CHCH : C(CH_3)COOR + C_2H_5MgBr \longrightarrow \\ &\qquad C_6H_5CH : CHCH : C(CH_3)COC_2H_5 + MgBrOR\end{aligned}$$

$$\begin{aligned}&C_6H_5CH : CHCH : C(CH_3)COC_2H_5 + C_2H_5MgBr \longrightarrow \\ &\qquad C_6H_5CH : CHCH : C(CH_3)C(C_2H_5)_2OH\end{aligned}$$

The results of the investigation with methyl α-methylcinnamylidenacetate and with the other esters of the series are given in the following table and for comparison the results with benzylidene compounds are added. Since in the experiments with cinnamylidene esters secondary reactions interfered to a great extent with the separation of the primary products, the yields obtained are not quantitative:

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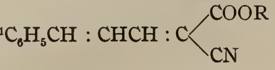
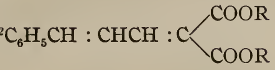
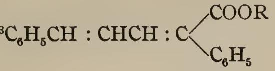
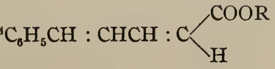
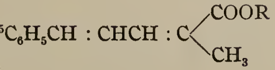
[1] Ber. d. chem. Ges., **21**, 3166; **24**, 1876.

	Magnesium compound	Per cent. of product formed by 1,4 addition	Per cent. of product formed by replacement of OR and 1,4 addition	Per cent. of product formed by replacement of OR and 1,2 addition
[1]  $C_6H_5CH : CHCH : C\left\langle\begin{matrix}COOR\\CN\end{matrix}\right.$	C_6H_5MgBr	100		
	C_2H_5MgBr	100		
[2]  $C_6H_5CH : CHCH : C\left\langle\begin{matrix}COOR\\COOR\end{matrix}\right.$	C_6H_5MgBr	95		
	CH_3MgI	76		
[3]  $C_6H_5CH : CHCH : C\left\langle\begin{matrix}COOR\\C_6H_5\end{matrix}\right.$	C_6H_5MgBr		87	
	CH_3MgI			100
[4]  $C_6H_5CH : CHCH : C\left\langle\begin{matrix}COOR\\H\end{matrix}\right.$	C_6H_5MgBr		79	
	C_2H_5MgBr			55
[5]  $C_6H_5CH : CHCH : C\left\langle\begin{matrix}COOR\\CH_3\end{matrix}\right.$	C_6H_5MgBr		100	
	C_2H_5MgBr			30

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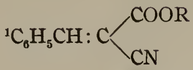
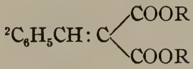
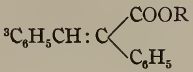
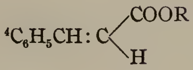
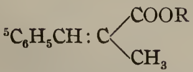
[1] Macleod: THIS JOURNAL, **44**, 331.

[2] Reimer: *Ibid.*, **38**, 227.

[3] Reimer and Reynolds: *Ibid.*, **40**, 428.

[4] Reynolds: *Ibid.*, **46**, 198.

[5] This paper.

	Magnesium compound	Per cent. of product formed by 1,4 addition	Per cent. of product formed by replacement of OR and 1,4 addition	Per cent. of product formed by replacement of OR and 1,2 addition
[1] $C_6H_5CH:C<^{COOR}_{CN}$	C_6H_5MgBr	100		
	CH_3MgI	100		
[2] $C_6H_5CH:C<^{COOR}_{COOR}$	C_6H_5MgBr	100		
	CH_3MgI	100		
[3] $C_6H_5CH:C<^{COOR}_{C_6H_5}$	C_6H_5MgBr	100		
	CH_3MgI			100
[4] $C_6H_5CH:C<^{COOR}_{H}$	C_6H_5MgBr	50	50	
	CH_3MgI			100
[5] $C_6H_5CH:C<^{COOR}_{CH_3}$	C_6H_5MgBr	4	96	
	CH_3MgI			100

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[1] Kohler and Reimer: THIS JOURNAL, **33**, 333.

[2] Kohler: *Ibid.*, **34**, 132.

[3] Kohler and Heritage: *Ibid.*, **33**, 153.

[4] Kohler and Heritage: *Ibid.*, **33**, 21.

[5] Kohler: *Ibid.*, **36**, 529.

It will be seen that the course of the reaction with esters that have a strongly positive or a strongly negative α-substituent is the same in both series. The reactions which differ in the two series are those with esters having a phenyl group or a hydrogen atom in the α position. In a previous paper[1] this anomalous behavior of methyl α-phenylcinnamylidenacetate was attributed to the spatial configuration of the ester. Subsequent work[2] with the isomeric esters of cinnamylidenacetic acid, however, did not bear out that explanation. No conclusion as to the cause of the difference in behavior of the α-phenyl and α-hydrogen esters in the two series can be reached until other isomeric cinnamylidene esters have been prepared and investigated.

EXPERIMENTAL

The α-methylcinnamylidenacetic acid used in this work was first prepared by Perkin's synthesis.[3] Later experiments showed that the tedious preparation of propionic anhydride might be avoided by heating at 160° for six hours a mixture of cinnamic aldehyde, propionyl chloride, and a large excess of sodium propionate. A 60 per cent. yield of acid was obtained by this method.

The methyl ester was prepared by boiling the acid in a 3 per cent. solution of hydrochloric acid in methyl alcohol for one hour. On cooling the ester separated from the solution in long, firm, colorless needles melting at 91°.

Reaction with Phenylmagnesium Bromide

In the first experiment two molecules of magnesium compound to one of the ester were used and the reaction carried out in cold, ethereal solution. When about one-half of the ester had reacted, a thick paste separated from the ether and any ester added after this point was recovered unchanged. It was found necessary to use at least four molecules of phenylmagnesium bromide to one of ester to avoid the separation of this pasty substance. After decomposition in the usual way, the product was boiled for one hour with dilute alcoholic potash to saponify any traces of ester that might have escaped reaction. After removal of the alcohol, the residue was extracted with water and the portion insoluble in water was distilled with steam to remove a considerable quantity of diphenyl. The residue was extracted with ether, the solution dried over calcium chloride, and the ester allowed to evaporate spontaneously. The product was a heavy, red oil from which there slowly separated a small quantity of needlelike crystals. These were filtered by suction and purified by repeated crystallization from methyl alcohol. The substance was found to be a ketone melting at 112°. A 17 per cent. yield was obtained. The oil was carefully fractioned under diminished pressure; there was some slight decomposition but most of the distillate boiled at 268° (10 mm.). Analyses of the oil gave the following results:

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[1] THIS JOURNAL, **40**, 430.

[2] *Ibid.*, **46**, 199.

[3] J. Chem. Soc., **31**, 406.

I. 0.1877 gram substance gave 0.6039 gram CO_2 and 0.1141 gram H_2O.

II. 0.1535 gram substance gave 0.4937 gram CO_2 and 0.0909 gram H_2O.

	Calculated for $C_{24}H_{22}O$	Found I	Found II
C	88.34	87.74	87.71
H	6.74	6.76	6.57

These analyses indicated that the oil was a mixture of isomeric ketones but no separation was effected.

The reaction was repeated but no larger yield of crystalline product could be obtained by this method. The experiment was then carried out with six molecules of magnesium compound for one of the ester. Instead of boiling the product with alcoholic potash, as in the previous reactions, it was treated with a cold dilute solution of that reagent. From 20 grams of ester 5 grams of the 112° ketone were obtained, a 16 per cent. yield. The oily residue, on treatment with cold methyl alcohol, gradually deposited 10 grams of a ketone, isomeric with the first, which melted at 85°. This was found to isomerize to the higher-melting ketone on boiling its alcoholic solution with hydrochloric acid or potassium hydroxide. The treatment of the product in the first experiments with boiling alcoholic potash had undoubtedly isomerized the low-melting ketone, at least partially, to the high-melting one, giving an oily mixture exceedingly difficult to separate. Accordingly, the experiment was repeated, omitting the treatment with alcoholic potash. The product was poured, in small quantities at a time, into cold methyl alcohol and the solid which separated was rapidly filtered with suction. It consisted almost entirely of low-melting ketone with only a trace of the high-melting isomer. The alcoholic filtrates deposited several grams of the oily product; the yield of the two solid ketones and the mixture was quantitative.

The amounts of the two ketones and of the oil varied greatly in different experiments so that it is impossible to give the relative quantities of each formed in the reaction. Attempts were made to determine the proportion of the two solid ketones by oxidation of the crude product of the Grignard reaction. This method was unsuccessful because benzoic acid was the only substance which could be isolated. Both ketones are soluble in methyl alcohol, the only solvent which could be used to affect their separation from the oil, and both dissolve readily in the oil itself. By careful manipulation of the mixture it was possible to separate, from time to time, small quantities of both ketones but nothing like a complete separation was ever accomplished. If this mixture was boiled with alcoholic potash, however, a considerable quantity of the high-melting ketone could be obtained; this method of procedure was subsequently adopted for the preparation of the quantities of this substance needed.

α-Methyl-β-phenyl-γ-benzalbutyrophenone (*112°*), $C_6H_5CH : CHCH(C_6H_5)CH(CH_3)COC_6H_5$.—The substance separates from boiling methyl alcohol in bunches of stiff, white needles. It is readily soluble in chloroform, acetone, benzene and ether, slightly soluble in ligroin and warm alcohol. It dissolves in concentrated sulphuric acid to give a brilliant orange solution.

Analysis:

I. 0.1643 gram substance gave 0.5283 gram CO_2 and 0.0963 gram H_2O.

II. 0.1792 gram substance gave 0.5772 gram CO_2 and 0.1094 gram H_2O.

	Calculated for $C_{24}H_{22}O$	Found I	Found II
C	88.34	88.00	87.90
H	6.74	6.39	6.78

Reaction with Phenylmagnesium Bromide. 2-Methyl-1,1,3,5-tetraphenyl-4-pentene-1-ol,

$$C_6H_5CH : CHCH(C_6H_5)CH(CH_3)C(C_6H_5)_2OH$$

—Four grams of ketone were dissolved in absolute ether and added to a solution of 6 grams of phenylmagnesium bromide cooled to 0°. A reaction took place at once, the magnesium compound separating as a white crystalline solid. The product was decomposed as usual; the ethereal solution deposited, on evaporation, a white solid which, after repeated crystallizations from hot methyl alcohol, separated in clear prisms which softened at 132° and melted at 150°. It was heated at 110° to free it of alcohol of crystallization and analyzed.

Analysis:

0.1465 gram substance gave 0.4796 gram CO_2 and 0.0932 gram H_2O.

	Calculated for $C_{30}H_{28}O$	Found
C	89.10	89.27
H	6.93	7.06

The compound is very soluble in ether, acetone, benzene, chloroform and boiling methyl and ethyl alcohols, slightly soluble in ligroin. It was proved to be a tertiary alcohol by treatment with ethylmagnesium bromide. A gas was evolved and after decomposition of the Grignard product the original substance was recovered unchanged.

The structure of the tertiary alcohol was established by oxidation. An acetone solution of 3.8 grams of the solid was treated at room temperature with finely powdered potassium permanganate as long as decolorization took place. The oxides of manganese were then separated by filtering with suction and the acetone allowed to evaporate spontaneously. The solid, deposited on complete removal of the solvent, was washed with cold methyl alcohol; 1.5 grams were obtained melting at 187°. Extraction of the oxides of manganese with boiling water gave a solution from which 0.5 gram of benzoic acid was precipitated. Finally the solution of the oxides of manganese in sulphuric acid, to which sulphur dioxide had been added, was extracted with ether. On evaporation of the ether, a mixture was left which was separated by treatment with cold methyl alcohol, 0.3 gram of benzoic acid dissolving in the methyl alcohol and 0.5 gram of the 187° solid remaining undissolved. This solid is very soluble in chloroform and acetone, only very slightly soluble in ether and methyl alcohol. It crystallizes in fine white needles from acetone, from a mixture of chloroform and methyl alcohol and from absolute alcohol.

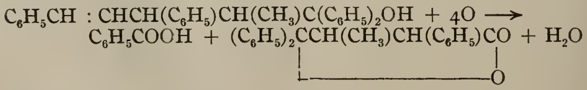
Analysis:

0.1528 gram substance gave 0.4720 gram CO_2 and 0.0830 gram H_2O.

	Calculated for $C_{23}H_{20}O_2$	Found
C	84.14	84.24
H	6.09	6.03

The substance is the lactone of *γ-hydroxytriphenylmethylbutyric acid*, formed by loss of one molecule of water from the γ-hydroxy acid which is a primary product of the reaction. It is insoluble in hot sodium carbonate and only very slightly soluble in aqueous potassium hydroxide. It dissolves readily, however, in potassium hydroxide to which a small amount of alcohol has been added. On evaporation of the alcohol and acidification of the ice-cold aqueous solution, the lactone is recovered unchanged.

The oxidation of the tertiary alcohol may be represented by the following equation



$$C_6H_5CH : CHCH(C_6H_5)CH(CH_3)C(C_6H_5)_2OH + 4O \longrightarrow C_6H_5COOH + (C_6H_5)_2\underset{|\!\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_O}{C}H(CH_3)CH(C_6H_5)CO + H_2O$$

Reaction with Bromine. Dibromo-α-methyl-β-phenyl-γ-benzalbutyrophenone, $C_6H_5CHBrCHBrCH(C_6H_5)CH(CH_3)COC_6H_5$.—Two grams of α-methyl-β-phenyl-γ-benzalbutyrophenone (112°)

were dissolved in chloroform and the solution cooled with ice. To this was added, drop by drop, a solution of one gram of bromine in chloroform. The solution was instantly decolorized. After standing for one hour the chloroform was allowed to evaporate spontaneously. The pasty product was dissolved in the smallest possible quantity of cold chloroform and twice the volume of methyl alcohol added. Fine, white needles separated rapidly; after several crystallizations, the substance melted with decomposition at 180°. The analysis shows the compound to be the dibromo addition product of the ketone.

Analysis:

0.1550 gram substance gave 0.3369 gram CO_2 and 0.0646 gram H_2O.

	Calculated for $C_{24}H_{22}OBr_2$	Found
C	59.25	59.27
H	4.52	4.63

The substance is very readily soluble in ether, chloroform, acetone and benzene, very slightly soluble in boiling alcohol.

The filtrate from which this bromine compound separated left, on evaporation, an oil and also a small quantity of a second crystalline compound. Repeated attempts to accumulate enough of this crystalline substance for analysis were unsuccessful. It separates from alcohol in soft, branching needles, melting at 115° and decomposing at about 180°. It was at first thought that this compound was a monobromide, formed by loss of hydrobromic acid from the dibromide, but as the latter substance could not be made to lose a molecule of hydrobromic acid under the most rigorous treatment, it is probable that the low-melting compound is an isomeric dibromo addition product of the ketone.

Oxidation of the Ketone (112°).—An acetone solution of the ketone was treated with powdered potassium permanganate; the reaction was so very slow that at the end of six hours a portion of the 2.3 grams of ketone used was not oxidized. The solution was filtered with suction and the acetone allowed to evaporate spontaneously; a very small amount of resinous material was left and also 0.6 gram of unchanged ketone. The oxides of manganese were extracted several times with boiling water. A mixture of two acids separated on acidifying the aqueous solution. The mixture was separated, though not completely, by taking advantage of the difference in solubility of the two acids in ligroin. By careful extraction with boiling ligroin benzoic acid was removed, and the portion left undissolved was purified by recrystallization from a mixture of chloroform and ligroin; it separates in fine white needles melting at 131°, is very soluble in chloroform, ether, methyl and ethyl alcohols, less soluble in ligroin and cold water.

Analysis:

0.1282 gram substance gave 0.3563 gram CO_2 and 0.0688 gram H_2O.

	Calculated for $C_{17}H_{16}O_3$	Found
C	76.11	75.80
H	5.97	5.96

The substance is *methylphenylbenzoylpropionic acid.* Its formation may be represented by the following equation:

$$C_6H_5CH : CHCH(C_6H_5)CH(CH_3)COC_6H_5 + 4O \longrightarrow C_6H_5COCH(CH_3)CH(C_6H_5)COOH + C_6H_5COOH$$

Methyl Methylphenylbenzoylpropionate, $C_6H_5COCH(CH_3)CH(C_6H_5)COOCH_3$.—The ester was prepared by treating 1.3 grams of acid with a saturated solution of hydrochloric acid in methyl alcohol. After standing overnight one gram of solid product separated; this was washed with cold methyl alcohol and crystallized from the same solvent. The ester separates in heavy plates melting at 105°; it is very soluble in chloroform, acetone, ether and warm methyl alcohol, very slightly soluble in ligroin.

Analysis:

0.1500 gram substance gave 0.4177 gram CO_2 and 0.0845 gram H_2O.

	Calculated for $C_{18}H_{18}O_3$	Found
C	76.59	75.94
H	6.38	6.26

A very small quantity of another ester, melting at 87°, was separated on complete evaporation of the solution but sufficient material was not obtained for analysis.

α-Methyl-β-phenyl-γ-benzalbutyrophenone (*85°*), $C_6H_5CH : CHCH(C_6H_5)CH(CH_3)COC_6H_5$.—This substance crystallizes from alcohol in stiff, white needles. It is very soluble in chloroform, ether, absolute alcohol, methyl alcohol, benzene and acetone, less soluble in ligroin. It dissolves in concentrated sulphuric acid to give a reddish yellow solution. It may be separated from its high-melting isomer by extracting the mixture repeatedly with cold absolute alcohol; from the solution it separates in thick needles melting at 85°.

Analysis:

I. 0.1416 gram substance gave 0.4560 gram CO_2 and 0.0860 gram H_2O.

II. 0.1622 gram substance gave 0.5233 gram CO_2 and 0.0985 gram H_2O.

	Calculated for $C_{24}H_{22}O$	Found I	II
C	88.34	87.80	87.98
H	6.74	6.74	6.74

A solution of this ketone in methyl alcohol containing dry hydrochloric acid was boiled for four hours. The solid which crystallized from the solution was almost pure high-melting ketone. This same isomerization was carried out by boiling the ketone or the oily mixture of ketones with potassium hydroxide in alcoholic solution. In this reaction there was always a residue which could not be made to solidify.

Reaction with Phenylmagnesium Bromide.—One and three-tenths grams of ketone, in ether solution, were treated with phenylmagnesium bromide cooled in ice water. The ethereal solution, obtained in the usual way, was allowed to evaporate spontaneously. The whole amount of ketone was recovered unchanged. The substances were then brought together in boiling ethereal solution and the mixture boiled for one hour. The ketone was again recovered unchanged.

Reaction with Bromine.—Seven-tenths of a gram of the ketone was dissolved in chloroform, the solution cooled to 0°

and 0.35 gram of bromine in chloroform added. Decolorization of the bromine took place at once. After the solvent had evaporated, the oily product remaining was dissolved in the least possible quantity of chloroform and twice the volume of methyl alcohol added. A small quantity of crystalline compound, melting with decomposition at 180°, was formed; it was found to be identical with the dibromo addition product of the high-melting ketone. From the yellowish oil, left after complete evaporation of the filtrate, no solid substance could be separated.

Since the isomerism of the ketones has been proved to be optical, the formation of this compound is evidently due to the isomerization of the low-melting to the high-melting ketone, under the influence of bromine or of a small quantity of hydrobromic acid formed in the reaction, and the formation from this of the dibromo compound already described.

Oxidation of the Ketone (85°).—The ketone was dissolved in acetone and treated with powdered potassium permanganate; decolorization took place rapidly and oxidation of 2 grams was complete in two hours. The solution was filtered at once and the oxides of manganese were repeatedly extracted with small quantities of boiling water. On acidifying the cold aqueous solution, an oily substance which solidified at once in contact with ligroin was precipitated. This product was a mixture of two acids which were completely separated by several extractions with boiling ligroin; the ligroin solution contained the entire yield of benzoic acid and a white solid remained undissolved. This insoluble acid was purified by recrystallization from a mixture of chloroform and ligroin, from which it separates in fine white needles melting at 145°. It is very soluble in chloroform, ether, benzene, methyl and ethyl alcohols, almost insoluble in ligroin and cold water.

Analysis:

0.1526 gram substance gave 0.4248 gram CO_2 and 0.0793 gram H_2O.

	Calculated for $C_{17}H_{16}O_3$	Found
C	76.11	75.92
H	5.97	5.77

The acid is *methylphenylbenzoylpropionic acid*, isomeric with the oxidation product obtained from the 112° ketone.

An ester was prepared by treating 1.3 grams of acid with a saturated solution of hydrochloric acid in methyl alcohol. On standing overnight, a quantitative yield of ester, melting at 105°, identical with that from the isomeric acid, separated from the solution. It is probable, therefore, that the low-melting ester, obtained only from the 131° acid, is the derivative of that acid and that the small yield of this ester and the large yield of the 105° ester obtained from the 131° acid may be due to the isomerization of that acid to the high-melting isomer under the influence of hydrochloric acid. This conclusion is borne out by the fact that on saponification of the 87° ester a mixture of the two acids results.

Reaction with Benzylmagnesium Bromide

An ethereal solution of 7 grams of methyl α-methylcinnamylidenacetate was allowed to react with a large excess of benzylmagnesium bromide. After a half hour the product was decomposed with iced hydrochloric acid, the solution extracted with ether, the ether evaporated, and the remaining yellow liquid distilled with steam until the dibenzyl was completely removed. The yellow product was extracted with ether and the ethereal extract dried. On evaporation of the solvent, 3.5 grams of solid separated. This was washed carefully with methyl alcohol and recrystallized from a mixture of chloroform and methyl alcohol, from which it separates in clusters of iridescent needles melting at 117°. It is very soluble in chloroform, less soluble in ligroin, ether and acetone, and only very slightly soluble in methyl and ethyl alcohols.

Analysis:

0.1590 gram substance gave 0.5395 gram CO_2 and 0.0995 gram H_2O.

	Calculated for $C_{26}H_{24}$	Found
C	92.85	92.53
H	7.14	6.95

The substance is *methylphenylbenzylbenzal-1,3-pentadiene*, formed by loss of one molecule of water from α,α-dibenzyl-β-methyl-δ-benzalcrotonyl alcohol:

$$C_6H_5CH:CHCH:C(CH_3)C(CH_2C_6H_5)_2OH \longrightarrow \\ C_6H_5CH:CHCH:C(CH_3)C(CH_2C_6H_5):CHC_6H_5$$

The structure of the hydrocarbon was established by oxidation. An acetone solution of 5 grams of the solid, cooled with ice water, was treated with finely powdered potassium permanganate until it was no longer decolorized. The solution was filtered and the acetone allowed to evaporate; no residue was left after complete removal of the solvent. The oxides of manganese were then extracted with boiling water; 2.7 grams of benzoic acid were precipitated from the aqueous solution. Also 2.4 grams of benzoic acid were obtained by dissolving the oxides in sulphuric acid, to which sulphur dioxide had been added, and extracting the solution with ether. The only other product of oxidation was a trace of phenylacetic acid. The reaction may be represented as follows:

$$C_6H_5CH : CHCH : C(CH_3)C(CH_2C_6H_5) : CHC_6H_5 \longrightarrow \\ 2C_6H_5COOH + C_6H_5CH_2COOH \longrightarrow 3C_6H_5COOH$$

Since complete oxidation of 5 grams of hydrocarbon should give 5.4 grams of benzoic acid, a yield of 5.1 grams of this acid indicates that the phenylacetic acid, which was first formed in the reaction, was subsequently almost entirely oxidized to form a third molecule of benzoic acid.

The product from the Grignard reaction which was not solid was heated for three hours with acetic anhydride in order that any α,α-dibenzyl-β-methyl-δ-benzalcrotonyl alcohol present might be decomposed. When the liquid was poured into water no hydrocarbon separated. Accordingly the yellow liquid was extracted with ether and the ethereal extract washed and dried over calcium chloride. After evaporation of the ether, the residue was distilled under diminished pressure; 8 grams of viscous, yellow liquid distilled at 265° (20 mm.).

Analysis:

0.1600 gram substance gave 0.5150 gram CO_2 and 0.0975 gram H_2O.

	Calculated for $C_{26}H_{26}O$	Found
C	88.13	87.88
H	7.34	6.77

The substance is *α-methyl-β-benzyl-γ-benzalpropyl benzyl ketone*, $C_6H_5CH : CHCH(CH_2C_6H_5)CH(CH_3)COCH_2C_6H_5$. When treated with ethylmagnesium bromide no gas was evolved; moreover, the ketone does not react with ethylmagnesium bromide, the original substance being recovered on decomposition of the Grignard product. This behavior indicates that the configuration of this ketone may be like that of the low-melting solid obtained in the reaction with phenylmagnesium bromide.

The ketone reacts readily with bromine, but a solid could not be separated from the dark brown product obtained.

The yield of ketone in the Grignard reaction with benzylmagnesium bromide was 65 per cent. and the yield of hydrocarbon 30 per cent.

Reaction with Ethylmagnesium Bromide

An ethereal solution of methyl α-methylcinnamylidenacetate was added slowly to a large excess of ethylmagnesium bromide until an oily layer began to separate from the ether. The reaction was then stopped and the Grignard product decomposed at once with iced hydrochloric acid; the solution was extracted with ether, the ethereal extract washed and dried over calcium chloride. The yellow liquid, left after removal of the ether, was distilled under diminished pressure. Its behavior indicated that it was a mixture, which apparently was not separated by distillation. Analyses of various fractions confirmed this assumption. Accordingly, the reaction was repeated and the product treated with cold aqueous potash and allowed to stand for a day. The alcohol was then evaporated in a current of air and the residue extracted with cold water. A small quantity of acid was precipitated from the aqueous solution. The portion insoluble in water was extracted with ether and the liquid, obtained after evaporation of the ether, was distilled under diminished pressure. This, likewise, did not behave like a pure substance and analyses of several fractions again indicated a mixture.

The procedure next adopted was to saponify the crude product by boiling with alcoholic potash. The alcohol was removed and the aqueous solution, obtained by extracting the residue with water, deposited, on acidification, several grams of acid. From the portion insoluble in water a lemon-yellow mobile liquid was separated which distilled constantly at 200° (20 mm.); 14.5 grams resulted from 43 grams of ester. Yield, 30 per cent.

Analysis:

0.1654 gram substance gave 0.5067 gram CO_2 and 0.01272 gram H_2O.

	Calculated for $C_{16}H_{22}O$	Found
C	83.47	83.54
H	9.56	8.54

The substance is *α, α-diethyl-β-methyl-δ-benzalcrotonyl alcohol*, $C_6H_5CH : CHCH : C(CH_3)C(C_2H_5)_2OH$. It was proved to be a hydroxyl compound by treatment with ethylmagnesium bromide. A gas was evolved and the original tertiary alcohol was recovered on decomposition of the Grignard product.

A high-boiling, viscous liquid, which distilled persistently with decomposition, was also separated by distillation under diminished pressure. On long standing this deposited an ester, melting at 185°, which was purified by crystallization from a mixture of ether and chloroform. Analyses indicated that it was not a primary product of the reaction.[1]

By saponification of the crude Grignard product from 43 grams of cinnamylidene ester, 12 grams of crude, yellow acid were obtained. This partially liquefied in the air and was very difficult to purify. About one gram of acid melting at 207° was finally separated pure by use of ligroin and methyl alcohol as solvents. Analyses, likewise, showed that this acid is not a primary product of the Grignard reaction. Neither this nor the ester were investigated further.

Since the corresponding tertiary alcohol obtained in the reaction with ethylmagnesium bromide and methylcinnamylidenacetate was almost completely decomposed by boiling with alcoholic potash,[2] it is possible that the course of procedure adopted in order to separate the α, α-diethyl-β-methyl-δ-benzalcrotonyl alcohol from the other products of the Grignard reaction may account for the small yield of tertiary alcohol separated.

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[1] Cf. This Journal, **34**, 568; **46**, 198.

[2] *Ibid.*, **46**, 211.

Chemical Laboratory
Barnard College
May, 1912

ACTION OF HEAT ON *p*-SULPHAMIDO-*o*-TOLUIC ACID

By John W. Nowell

The work of Hartman, Muckenfuss, Stoddard, Chamberlain, Simmons and Rouiller[1] has shown that in the peculiar change undergone by *p*-sulphamidobenzoic acid when it is heated several hours at 220° one of the resulting products is *p*-sulphobenzamidine, $HO_3SC_6H_4C(:NH)NH_2$, or its inner salt. Nakaseko[2] found that *m*-sulphamidobenzoic acid, in which the sulphonic and carboxylic groups are in the meta instead of the para position to each other, gives an analogous product, and Chamberlain[3] likewise showed this to be true of *p*-sulphamido-*m*-toluic acid, in which the meta position to the carboxyl is occupied by a methyl group. Inasmuch as *o*-substituted amidines cannot be obtained by the Pinner method and Rouiller found no indication of the formation of such a compound by his method when applied to *o*-nitrobenzoic acid, although the *m*- and *p*-acids reacted smoothly,[4] it became of interest to determine whether substituents in the ortho position to the carboxylic group in *p*-sulphamidobenzoic acid would prevent the formation of an amidine. In the one case studied, viz., that of *p*-sulphamido-*o*-toluic acid, such was found to be the case; the only products obtained were acid ammonium *p*-sulpho-*o*-toluate and carbamido-*o*-toluene-*p*-sulphonic acid. Rouiller has shown that carboxamides are probably intermediate products in the formation of amidines from carboxylic acids and sulphonamides,[1] and it therefore appears that the effect of the *o*-methyl group has been to arrest the reaction at this intermediate stage.

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[1] For a summary of this work, see This Journal, **47**, 475.

[2] *Ibid.*, **47**, 429.

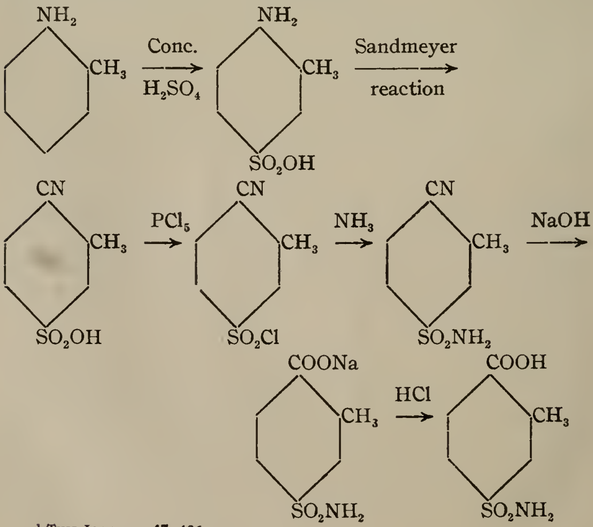
[3] *Ibid.*, **47**, 333.

[4] *Ibid.*, **47**, 490. In the case of the *o*-acid, no attempt was made to isolate an amidine, as the product, on distillation with magnesium and sodium hydroxides, successively, lost, as ammonia, 61.3 per cent. of the nitrogen originally present as benzenesulphonamide with the magnesium hydroxide, and only 3.5 per cent. with the sodium hydroxide, whereas any amidine, if formed, should lose equal amounts of nitrogen with each reagent. It was concluded, therefore, that practically nothing but an ammonium salt was formed. It may be, however, that the nitro group in the *o*-position prevented the hydrolysis of any amidine which might have been formed. The experiment will be repeated on a larger scale and an attempt made to isolate all the products formed.—C. A. R.

Attempts were made to prepare other *o*-substituted *p*-sulphamidobenzoic acids, but the difficulties encountered were so great that this could not be done in the time at the author's disposal.

Preparation of Material

On looking into the literature, it was found that Jacobsen[2] had prepared *p*-sulphamido-*o*-toluic acid by oxidizing *p*-sulphamido-*o*-xylene, but in view of the fact that *o*-xylene is rather costly and difficult to obtain in sufficient quantities, the following method for preparing *p*-sulphamido-*o*-toluic acid was tried and found to be very satisfactory:



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[1] This Journal, **47**, 486.

[2] Ber. d. chem. Ges., **11**, 22; **14**, 39.

p-Sulpho-*o*-toluidine, prepared according to the directions of Neville and Winther,[1] was diazotized in the usual manner. The diazotized product precipitated out of solution so I filtered it off and added it, suspended in water, to the cuprous cyanide solution. When the solution had cooled, I added hydrochloric acid and a dirty, yellowish gray precipitate came down, consisting chiefly of copper salts. This clayey looking precipitate was filtered off and the solution concentrated to about one-third its volume. On cooling, the potassium salt of *p*-sulpho-*o*-tolunitrile crystallized out in long silky needles and from more concentrated solutions in rosettes with needles radiating from the center. The last portions were extracted with boiling alcohol to separate the nitrile from inorganic salts. Yield, about 90 per cent. of the theoretical.

Preparation of the Chloride of p-*Sulpho*-o-*tolunitrile*.—The above potassium salt was treated with its own weight of phosphorus pentachloride (slightly more than one molecule), and rubbed up in a mortar, when a vigorous reaction took place and the whole mass melted to a thick, brownish yellow liquid. The product was heated for some time on the water bath to drive off all fumes and to complete the reaction. When cool, it was washed with ice water, generally about six or seven times, to take out all inorganic salts. The product crystallized from ligroin in beautiful, colorless crystals, mostly diamond-shaped or rather elongated diamonds with striations on the faces, melting at 52°.5–53°. Yield, about 50 per cent.

Preparation of p-*Sulphamido*-o-*tolunitrile*.—The crude acid chloride, after being washed about six times with ice water, was treated with concentrated ammonia. When stirred vigorously, a very noticeable reaction set in and in a short time all the acid chloride dissolved, leaving a clear, brownish yellow solution. On concentrating to a small volume, which eliminated the excess of ammonia, the *p*-sulphamido-*o*-tolunitrile came down in brownish fluffy crystals which, after boiling with charcoal, separated in long crystals with rough edges somewhat like saw teeth. After several recrystallizations, the crystals still had a slight yellowish color but the melting point was constant at 159°–160°. Yield, about 75 per cent.

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[1] Ber. d. chem. Ges., **13**, 1940.

Preparation of p-*Sulphamido*-o-*toluic Acid.*—The *p*-sulphamido-*o*-tolunitrile was digested for six hours with an excess of caustic soda. There was a copious evolution of ammonia. When the reaction was complete, the solution was cooled and acidified with hydrochloric acid, when the whole mass almost solidified, so fine and silky were the crystals. After five crystallizations, the acid came out in beautiful colorless, silky needles, melting at 211°. From five hundred grams of *o*-toluidine I obtained one hundred and fifty grams of the crystallized acid.

Analyses:

0.3643 gram heated two hours at 109° lost 0.0004 gram.

0.3643 gram heated two hours at 150° gained 0.0013 gram.

0.5057 gram heated two hours at 145° gained 0.0001 gram.

From the above results it is evident that *p*-sulphamido-*o*-toluic acid contains no water of crystallization.

0.6066 gram of the acid required 28.25 cc. of 0.1 N alkali to neutralize it.

0.5741 gram of the acid required 26.72 cc. of 0.1 N alkali to neutralize it.

	Calculated for $CH_3C_6H_3(SO_2NH_2)COOH$	Found I	II
Molecular weight	215.15	214.72	214.85

0.1994 gram gave 0.2105 gram $BaSO_4$ (Liebig).

0.2270 gram gave 0.2485 gram $BaSO_4$ (Liebig).

	Calculated for $CH_3C_6H_3(SO_2NH_2)COOH$	Found I	II
S	14.9	14.5	15.03

Potassium Salt.—This salt was prepared by neutralizing 5 grams of *p*-sulphamido-*o*-toluic acid with potassium hydroxide and evaporating to crystallization, when it came out in beautiful colorless, glasslike crystals. It has been described by Jacobsen[1] as glassy prisms of rhombohedral habit.

Analyses:

0.6362 gram lost 0.0222 gram of water at 150°.

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[1] Ber. d. chem. Ges., **14**, 39.

0.6002 gram lost 0.0207 gram of water at 150°.
0.6140 gram gave 0.2057 gram K_2SO_4.
0.5795 gram gave 0.1938 gram K_2SO_4.

	Calculated for $CH_3C_6H_3(SO_2NH_2)COOK + 0.5H_2O$	Found I	II
K	14.89	15.03	15.00
H_2O	3.43	3.44	3.48

Ammonium Salt.—By treating *p*-sulphamido-*o*-toluic acid with ammonia, a substance was obtained which crystallized easily from concentrated water solutions in crystals like elongated diamonds melting at 169°–172°. In no case was the melting point sharp at all.

0.4224 gram gave with $Mg(OH)_2$ ammonia equivalent to 16.9 cc. 0.1 cc. 0.1 N acid.

0.5246 gram lost 0.041 gram at 120°

	Calculated for $CH_3C_6H_3(SO_2NH_2)COONH .H_2O$	Found
0.5 N	5.60	5.60
H_2O	7.20	7.81

Preparation of Acid Ammonium p-*Sulpho*-o-*toluate.*—Following Waters' method[1] for preparing his acid ammonium salt, ten grams of *p*-sulphamido-*o*-toluic acid were mixed in a sealed tube with 20 cc. of concentrated hydrochloric acid and heated at 200° for ten hours. On removal of the tube from the furnace, small prismatic crystals were observed all through the mass. The contents of the tube were dissolved in water and on concentrating the solution, prismatic crystals melting at 285°–288° were obtained. After about six crystallizations from water, I obtained crystals having a melting point of 288°–289°. The salt was identical with that obtained by heating the sulphamido acid at 220° (see p. 238).

Attempt to Prepare the Diammonium Salt of p-*Sulpho*-o-*toluic Acid.*—I hydrolyzed potassium *p*-sulpho-*o*-tolunitrile with caustic potash, then saturated an alcoholic solution of the resulting salt with hydrochloric acid gas, when the potassium chloride was precipitated out and the filtered solution evaporated to dryness to remove the hydrochloric acid. The free *p*-sulpho-*o*-toluic acid was now neutralized with ammonia but I was never able to get the diammonium salt out pure enough for analysis, because it is hydrolyzed so easily. By recrystallizing from acetone, I obtained shiny grains melting at 211°–215°. From water it came down as long, slender prisms at first, about half of which melted at 215°, and the remainder at 269°–271°. On standing overnight the bottom of the beaker became covered with short, thick prisms, identical in appearance with the acid ammonium salt and which showed no signs of melting till 275° was reached. The solution had also become distinctly acid, proving conclusively that the diammonium salt was being hydrolyzed to the acid ammonium salt. No analysis was made, as crystals of a definite melting point were not obtained. See also page 237 for the analogous behavior of the solution of the product obtained by heating *p*-sulphamido-*o*-toluic acid and then neutralizing with ammonia.

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[1] Diss., Johns Hopkins Univ., **1899**, p. 28. THIS JOURNAL, **47**, 349.

Waters[1] encountered the same difficulty in trying to prepare the diammonium salt of *p*-sulpho-*m*-toluic acid by precipitating exactly the barium from a solution of the sulphotoluate by means of ammonium sulphate. Instead of obtaining the diammonium salt, he obtained only the acid ammonium salt. He says that "this surprising result could be due only to a loss of ammonia on evaporating the solution."

Preparation of the Acid Barium p-*Sulpho*-o-*toluate*.—Thirty grams of the product obtained by heating *p*-sulphamido-*o*-toluic acid (see page 236) were dissolved in water and divided into two equal parts. One part was just neutralized with barium hydroxide and then added to the other half of the solution. On standing overnight a grayish powder came down and, over it, some clusters of needles very soluble in water. When boiled with charcoal and recrystallized from water, the substance came out in small, shiny, silky plates which showed no signs of melting up to 300°. After several recrystallizations from water, I obtained pure white needles arranged mostly in rosettes which, when dried, had a leafy, glassy appearance.

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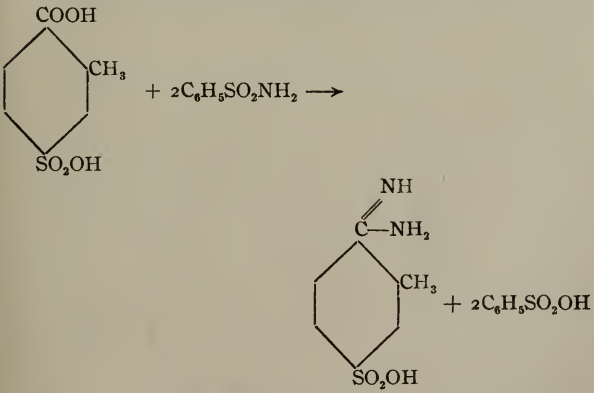
[1] Diss., Johns Hopkins Univ., **1899**, p. 28.

Analyses:

0.4188 gram gave 0.1635 gram $BaSO_4$ (Liebig).
0.4256 gram gave 0.1653 gram $BaSO_4$ (Liebig).
0.3091 gram lost 0.0182 gram when heated 8 hours at 175°.

	Calculated for $\left(CH_3C_6H_3\begin{smallmatrix}COOH\\ SO_3\end{smallmatrix}\right)_2Ba.2H_2O$	Found
Ba	22.77	22.85–22.97
H_2O	5.96	5.88

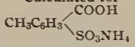
Attempt to Prepare p-*Sulpho*-o-*toluamidine.*—*p*-Sulpho-*o*-toluic acid was made by digesting *p*-sulpho-*o*-tolunitrile with an excess of barium hydroxide, till hydrolysis was complete, then the barium was exactly precipitated with sulphuric acid and the filtered solution evaporated to dryness, when the free sulphotoluic acid was obtained as a white amorphous powder. By heating *p*-sulpho-*o*-toluic acid with benzenesulphonamide, I hoped to obtain the amidine by the following reaction:

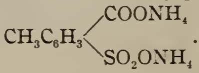


Twelve grams of the acid and eighteen grams of benzenesulphonamide were thoroughly mixed and heated in a sealed tube for two and one-half hours at 225°. The mixture melted to a dark brown mass which was readily soluble in cold water except for a trace of carbonaceous matter. The solution was extracted three times with 25 cc. portions of ether and on evaporating the ether extract, there remained a few oily drops which had a distinct nitrile odor and gave off ammonia with sodium hydroxide. The water solution was just neutralized with barium hydroxide and evaporated to dryness. I then extracted the dry residue with absolute alcohol that I might separate the barium salts from the products soluble in alcohol.

Alcoholic Extract.—When evaporated to crystallization, the alcoholic solution deposited an amorphous powder melting at 245°–275°. I was never able to get any characteristic crystals. After three recrystallizations, the substance melted at 270°–290° and gave off about twice as much ammonia with magnesium hydroxide as with sodium hydroxide, though the amount of ammonia was far too small for the acid ammonium salt.

0.3405 gram gave with $Mg(OH)_2$ ammonia equal to 2.7 cc. 0.1 N acid and with NaOH ammonia equal to 1.15 cc. 0.1 N acid.

	Calculated for  $CH_3C_6H_3\left\langle\begin{array}{l}COOH\\ SO_3NH_4\end{array}\right.$	Found
N	6.01	1.58

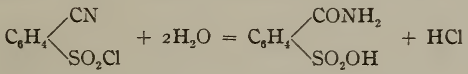
Substance Insoluble in Alcohol.—The portion insoluble in alcohol was treated with ammonium sulphate till the barium was just precipitated, the barium sulphate filtered off and the solution evaporated to dryness. The dried residue was then dissolved in alcohol and precipitated with ether, by which method I obtained an amorphous powder melting at 240°–252°. The ammonia liberated from this substance by boiling 0.250 gram with magnesium hydroxide neutralized 18.6 cc. 0.1 N acid and that set free by caustic soda neutralized only 0.45 cc. 0.1 N acid, so it is evident that the nitrogen is present in the form of ammonium salts, very probably a mixture of $C_6H_5SO_3NH_4$ and  $CH_3C_6H_3\left\langle\begin{array}{l}COONH_4\\ SO_2ONH_4\end{array}\right.$. Not a trace of amidine was found.

*Attempts to Prepare Carbamido-*o*-toluene-*p*-sulphonic Acid.*—

The method of Radziszewski[1] for obtaining amides from nitriles by the action of hydrogen peroxide was first tried. Potassium *p*-sulpho-*o*-tolunitrile was treated with a slightly alkaline solution of hydrogen peroxide and warmed on the water bath at 40° till the evolution of gas ceased. On concentration, the solution deposited only an amorphous powder which, when treated with ammonia, gave a substance melting at 185°–195°, chiefly the diammonium salt of *p*-sulpho-*o*-toluic acid, showing that the nitrile group was saponified completely to the carboxyl group, yielding only *p*-sulpho-*o*-toluic acid.

Simmons[2] found the same thing in the case of *p*-sulphobenzonitrile, for when he treated the nitrile with alkaline hydrogen peroxide, he got only *p*-sulphobenzoic acid.

I next tried the method of Jesurun,[3] who obtained *p*-sulphobenzamide by the following reaction:



$$C_6H_4\begin{cases}CN\\SO_2Cl\end{cases} + 2H_2O = C_6H_4\begin{cases}CONH_2\\SO_2OH\end{cases} + HCl$$

the reaction taking place in a sealed tube at 95°–100°. Five grams of potassium *p*-sulpho-*o*-tolunitrile with 5 cc. of 0.1 N sulphuric acid were heated in a sealed tube for five hours at 100°. When the tube was opened and the contents evaporated to crystallization, I obtained the original nitrile unchanged.

The successful method for preparing the carbamido-*o*-toluene-*p*-sulphonic acid was finally discovered accidentally. All attempts to prepare the free sulphotolunitrile from the potassium salt by dissolving it in water and acidifying with hydrochloric acid having failed, I dissolved the salt in absolute alcohol and saturated the solution with dry hydrogen chloride gas, hoping thus to throw out the potassium as potassium chloride and obtain the free *p*-sulpho-*o*-tolunitrile. During the process the temperature was allowed to rise almost to the boiling point of the alcohol. The potassium chloride was filtered off and the alcoholic solution evaporated to a small volume but nothing would crystallize out, so I evaporated the

[1] Ber. d. chem. Ges., **18**, 355.

[2] Diss., Johns Hopkins University, **1901**.

[3] Ber. d. chem. Ges., **26**, 2289.

solution to dryness and heated the residues on the water bath till all the hydrochloric acid was expelled. The residue was strongly acid. It was neutralized with ammonia and on crystallization I obtained beautiful, long, prismatic crystals melting at 276°–278°.

Analysis:

0.3081 gram gave with $Mg(OH)_2$ ammonia equivalent to 13.1 cc. 0.1 N acid, and with NaOH ammonia equivalent to 13.6 cc. 0.1 N acid.

	Calculated for		Found	
	$CH_3C_6H_3(CN)SO_3NH_4$	$CH_3C_6H_3(CONH_2)SO_3NH_4$	$Mg(OH)_2$	NaOH
0.5 N	6.54	6.03	5.95	6.18

Preparation of the Barium Salt—Another portion of the acid residue was neutralized with barium hydroxide, and after several crystallizations I was able to get out the barium salt reasonably pure.

Analysis:

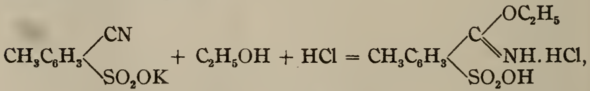
0.5183 gram lost 0.0283 gram at 200°.

0.6933 gram gave 0.2687 gram $BaSO_4$.

0.3224 gram gave 0.1250 gram $BaSO_4$.

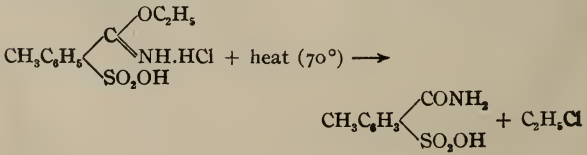
	Calculated for	Found	
	$[CH_3C_6H_3(CONH_2)SO_3]_2Ba.2H_2O$	I	II
Ba	22.84	22.80	22.81
H_2O	5.99	5.46	...

From the above analyses of the ammonium and barium salts of this acid it seems very probable that the following reaction has taken place:



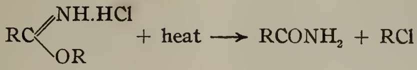
$$CH_3C_6H_3\begin{cases}CN\\SO_2OK\end{cases} + C_2H_5OH + HCl = CH_3C_6H_3\begin{cases}C\begin{cases}OC_2H_5\\NH.HCl,\end{cases}\\SO_2OH\end{cases}$$

and that the imido ester at the temperature of the reaction breaks up as follows:



$$CH_3C_6H_5\begin{cases}C\begin{cases}OC_2H_5\\NH.HCl\end{cases}\\SO_2OH\end{cases} + \text{heat } (70°) \longrightarrow CH_3C_6H_3\begin{cases}CONH_2\\SO_2OH\end{cases} + C_2H_5Cl$$

Pinner[1] says that imido esters in the solid state break down as follows when heated:



$$RC\begin{cases}NH.HCl\\OR\end{cases} + \text{heat} \longrightarrow RCONH_2 + RCl$$

so to satisfy myself that the same reaction takes place in alcohol when the temperature is allowed to rise nearly to the boiling point, I tested benzonitrile in the same way as the sulphotolunitrile above and though I obtained some ammonium chloride, I also was able to isolate quite a considerable amount of benzamide. The ammonium chloride, being insoluble in absolute alcohol, was filtered off and on concentrating the alcoholic solution a white crystalline substance came out having a melting point of 128°, identical with that of benzamide, and when mixed with benzamide the melting point remained constant. Judging from the analyses of the two salts and the analogous experiment with benzonitrile, it is pretty conclusively shown that by treating an alcoholic solution of potassium *p*-sulpho-*o*-tolunitrile with hydrochloric acid gas, there is formed, not *p*-sulpho-*o*-tolunitrile, but 1-carbamido-2-methylbenzene-4-sulphonic acid.

Determination of the Most Suitable Conditions for Heating p-*Sulphamido*-o-*toluic Acid.*—Since *p*-sulphamido-*o*-toluic acid does not lose any of its nitrogen when boiled with either magnesium hydroxide or caustic soda while amidines lose one atom of nitrogen as ammonia when boiled with magnesium hydroxide and another atom when boiled with caustic soda, it was thought that by boiling successively with these two reagents the product obtained by heating the acid at various temperatures and different lengths of time some indication might be obtained as to the extent of any reaction which might have taken place similar to that observed in the case of *m*- and *p*-sulphamidobenzoic and *p*-sulphamido-*m*-toluic acids, and that in this way the most favorable conditions for heating the acid in larger quantities might be determined.

I. 0.4850 gram heated in a sealed tube two hours at 220°

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[1] Die Imido-aether, p. 5.

gave with $Mg(OH)_2$ 48.59 per cent. nitrogen; with NaOH 42.96 per cent. nitrogen.

II. 0.4484 gram heated in a sealed tube four hours at 220° gave with $Mg(OH)_2$ 47.71 per cent. nitrogen; with NaOH 40.44 per cent. nitrogen.

III. 0.4999 gram heated in a sealed tube six hours at 240° gave with $Mg(OH)_2$ 56.80 per cent. nitrogen; with NaOH 23.26 per cent. nitrogen.

From the above tests it appears that two hours' heating at 220° is the most favorable condition for preparing the melt of *p*-sulphamido-*o*-toluic acid.

Preparation of the Melt.—The heating was carried out in a large paraffin bath, the temperature of which could be kept constant to within 2°–3° for a long time.

Test tubes, each containing ten grams of acid and closed loosely with a cork stopper, were heated for two hours at 220° and then allowed to cool in the air. Unlike the melt from *p*-sulphamido-*m*-toluic acid, that from *p*-sulphamido-*o*-toluic acid showed no signs of deliquescence at all. When cool the tubes were broken and the melt removed. The melt was now a dark, brown, brittle mass, very shiny and resembling sealing wax somewhat. When the tubes were opened there was always a distinct nitrile odor and around the the top of each tube was observed a very small amount of a sublimate which had the same melting point as the original acid and, when mixed with the acid, still melted at the same temperature, indicating that the sublimate was unchanged *p*-sulphamido-*o*-toluic acid.

Treatment of the Melt.—The first three melts were worked with the main idea of isolating first any "infusible diamide" which might have been formed. Several portions of the melt were subjected to different methods of treatment, so it might not be out of place to give each method separately.

I. Twenty grams of the melt were ground up in a mortar and extracted with cold water until all the substance had dissolved, giving a reddish brown solution, slightly milky in appearance. Unlike the melts of previous workers, the melt of *p*-sulphamido-*o*-toluic acid was completely soluble in a relatively small quantity of cold water. On standing overnight, a very small amount of a flocculent substance settled out which was soluble in alkalies and reprecipitated by acids. The amount of the substance was far too small for analysis and I never again obtained any of the substance from the other melts.

The clear filtrate was now evaporated to dryness and extracted with acetone.

a. Acetone Extract.—Only a very small portion of the melt was soluble in acetone. On evaporating off the acetone, small, light yellow nodules, having a melting point of 192°–200°, settled to the bottom. When recrystallized from water, it melted at 165°–170°. The amount of substance was too small to purify for analysis.

b. Substance Insoluble in Acetone.—The greater portion of the melt was insoluble in acetone, so it was crystallized several times from water, when short, prismatic needles were formed, some arranging themselves as rosettes and some as crosses. They melted at 285°–288°, which is the same as the melting point of acid ammonium *p*-sulpho-*o*-toluate (p. 227) and, when mixed with the synthetic acid salt, the melting point was unchanged, proving the identity of the two substances.

II. Thirty grams of the melt was ground up in a mortar with a small amount of cold water, when all the substance went into solution readily. The water solution was extracted three times with ether and on evaporation of the ether extract a few oily drops were obtained which had a distinct nitrile odor and gave off ammonia freely with caustic soda.

The filtrate was evaporated to dryness and extracted with acetone.

a. Acetone Extract.—On evaporation of the acetone extract, nothing came down except a black tarry mass from which I was unable to isolate any definite product.

b. Substance Insoluble in Acetone.—The part insoluble in acetone was dissolved in water and just enough barium hydroxide added to neutralize the solution, which was then evaporated to dryness and the residue extracted with absolute alcohol to separate the barium salts from other salts.

1. The alcoholic extract, on concentration, gave a white

amorphous powder which gave off ammonia freely with caustic soda. When recrystallized, it came down in prismatic plates and crosses melting at 242°–248°. It was probably the impure acid ammonium salt.

2. The barium salts, insoluble in alcohol, yielded only a grayish powder which was never obtained pure enough for analysis. In another experiment (see p. 228), half of the solution of the melt in water was neutralized with barium hydroxide and added to the other half of the solution. On concentrating, acid barium *p*-sulpho-*o*-toluate crystallized out.

III. Twenty grams of the melt were next treated according to Nakaseko's[1] plan for the separation of the products of the melt. The melt was ground up in a mortar and extracted three times with ether. The ether extract yielded a few oily drops which had a distinct nitrile odor and gave off ammonia freely with caustic soda. The melt was then extracted four times with acetone, which was considerably colored by the dissolved substance.

a. The acetone extract on concentration yielded only a black tarry mass from which no definite product was isolated.

b. Portion Insoluble in Acetone.—The residue, which was about 95 per cent. of the whole melt, was dissolved in 50 cc. of water. The beaker was then set aside in a vacuum desiccator over sulphuric acid and allowed to stand until crystallization began. The substance came down first in the form of an amorphous powder melting at 270°–274°, evidently impure acid ammonium salt. I tried recrystallization by the above method several times but was never able to get any distinct crystals. I then tried recrystallization from alcohol in a vacuum but was able to get no better results.

Having by the above methods been able to isolate only acid ammonium and barium sulphotoluates, I next treated the melt as follows:

IV. I heated twenty grams of *p*-sulphamido-*o*-toluic acid two hours at 223°. On cooling, the dark brown brittle mass had a distinct nitrile odor. It was dissolved in about 50 cc. of water and digested with charcoal to remove the brown color. To the now clear solution of the melt, 0.2 N ammonia was added until it was just neutral. Four hundred cc. of the ammonia was required and as 465 cc. would have been necessary to neutralize the original acid, it is evident that the acidity is practically the same after as before the heating. The neutral solution was concentrated to about one-half its volume and on standing overnight a mass of prismatic crystals came down, so thick that the beaker could be inverted without any of the solution spilling. After four crystallizations, the substance came out in shiny, needlelike, elongated prisms melting at 274°–276°.5, and when mixed with some of the ammonium 1-carbamido-2-methylbenzene-4-sulphonate described above (p. 232), the melting point was unchanged, this fact, of itself, pointing to the identity of the two compounds.

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[1] Diss., Johns Hopkins Univ., **1899**. THIS JOURNAL, **47**, 429.

Analysis of the crystals melting at 274°–276°.5:

0.2686 gram boiled with $Mg(OH)_2$ gave ammonia equal to 11.5 cc. 0.1 N acid; and with NaOH gave ammonia equal to 11.5 cc. 0.1 N acid.

	Calculated for $CH_3C_6H_3(CONH_2)SO_2ONH_4$	Found
With $Mg(OH)_2$ N	6.035	5.99
With NaOH N	6.035	6.16
Total N	12.07	12.15

So, without a doubt, the substance in the melt that gave this ammonium salt was 1-carbamido-2-methylbenzene-4-sulphonic acid.

After filtering off the prismatic crystals described above, the mother liquor was further concentrated and the whole mass solidified without crystallizing at all. Part of it was dissolved in acetone and a substance melting at 210°–220°, evidently the diammonium salt of *p*-sulpho-*o*-toluic acid, separated but could not be obtained in pure form. I then dissolved it in 95 per cent. alcohol and let it stand, when transparent needles or elongated prisms grouped in the form of rosettes and melting at 284°–286° came out. Analysis of this fraction gave 8.18 per cent. nitrogen, which is between the calculated values for the acid, 6.01 per cent., and diammonium, 11.2 per cent., salts, showing very plainly that I had here a mixture of the two salts.

On standing for a day or more, the final mother liquor deposited colorless stout prisms and cubes which melted at 284°–284°.5.

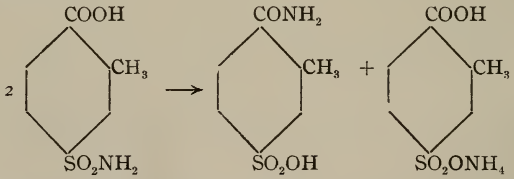
Analysis:

0.3018 gram gave with $Mg(OH)_2$ ammonia equivalent to 13.00 cc. 0.1 N acid; and with NaOH only a trace.

	Calculated for $CH_3C_6H_3(COOH)SO_2ONH_4$	Found
N	6.01	6.03

The final mother liquor was distinctly acid to litmus, showing that the diammonium salt is quickly hydrolyzed to the acid ammonium salt.

Having isolated only acid ammonium sulphotoluate and ammonium 1-carbamido-2-methyl-4-sulphotoluate from the melts, the course of the reaction that takes place when *p*-sulphamido-*o*-toluic acid is heated to 220° for two hours may be represented thus:

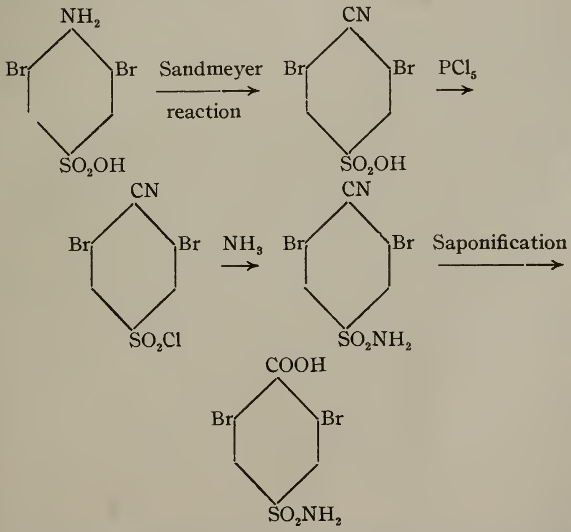


indicating that the methyl group in the ortho position to the carboxyl in *p*-sulphamido-*o*-toluic acid exercises a steric hindrance effect, arresting the reaction at an intermediate stage and preventing entirely the formation of an amidine.

The water necessary for the formation of the acid ammonium sulphotoluate is doubtless furnished by the carbonization of a part of the acid. That the reaction proceeds essentially as represented above is indicated by the fact that the total acidity is practically unchanged and that approximately one-half of the total nitrogen is set free from the reaction product by magnesium hydroxide and the other half by sodium hydroxide (see Experiment I, p. 233).

Having tested out the effect of a methyl group in the ortho position to the carboxyl, attempts were now made to prepare other compounds with different substituent groups in the ortho position to the carboxyl group in *p*-sulphamidobenzoic acid that the relative steric hindrance effect of different substituent groups might be compared.

Attempt to Prepare 2,6-Dibromo-4-sulphamidobenzoic Acid.—Barium 2,6-dibromosulphanilate was prepared according to the directions given by Heinichen.[1] I hoped now by the following reactions to pass from the 2,6-dibromosulphanilic acid to 2,6-dibromo-4-sulphamidobenzoic acid:



I precipitated the barium from the barium salt with a slight excess of sulphuric acid, filtered off the barium sulphate and subjected the clear solution to the "Sandmeyer Reaction." On concentrating and cooling, a kind of jellylike, greenish mass came down which, when recrystallized from water, deposited a network of long yellow needles. The needles, however, were so very soluble in water that I made the barium salt which came out in fine shiny plates forming a fluffy mass. These were purified by recrystallization and dried for analysis, but the ammonia given off by 0.8437 gram of the salt when distilled for three hours with an excess of caustic soda only neutralized 0.6 cc. of 0.1 N acid. From this, it is evident that the salt is either not a nitrile or if it is a nitrile, the two bromine groups in the ortho positions prevent saponification. In view of this fact, further attempts to prepare 2,6-dibromo-4-sulphamidobenzoic acid were abandoned for the time being.

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[1] Ann. Chem. (Liebig), **253**, 269.

Preparation of o-*Nitro*-p-*sulphamidobenzoic Acid.*—An attempt was now made to prepare *o*-nitrosulphanilic acid according to the directions given by Nietzki and Lerch.[1] One part of acetanilide was treated with three parts of fuming sulphuric acid containing 18–20 per cent. of sulphur trioxide. Then two parts of concentrated sulphuric acid were added. The calculated amount of concentrated nitric acid, mixed with an equal volume of sulphuric acid, was dropped in slowly with constant shaking. When cooled, the mixture was poured on ice, when a broth of yellow needles should separate, the acetyl group being split off by the water. In no case, however, was I able to get any yellow needles of *o*-nitrosulphanilic acid by this method, so I turned to another method for preparing *o*-nitro-*p*-sulphamidobenzoic acid.

I began with *o*-nitrotoluene as the starting point and followed Hart's[2] directions for getting calcium *o*-nitrotoluene-*p*-sulphonate. The calcium salt was changed into the potassium salt by treating it with potassium sulphate and filtering off the calcium sulphate formed. On cooling the filtrate, the potassium salt came out in long, prismatic needles, which were dried and treated with phosphorus pentachloride. On heating the mixture on the water bath, a reaction set in and the whole mass melted to a light yellow liquid, which was washed several times with ice water and then treated with concentrated ammonia until all the substance had gone into solution. On evaporating off the excess of ammonia and decolorizing the solution with charcoal, the amide came out in fine, silky needles melting at 120°–125° after one crystallization. By repeated crystallization from water, I obtained the amide melting at 142°–143°, which was comparatively pure.

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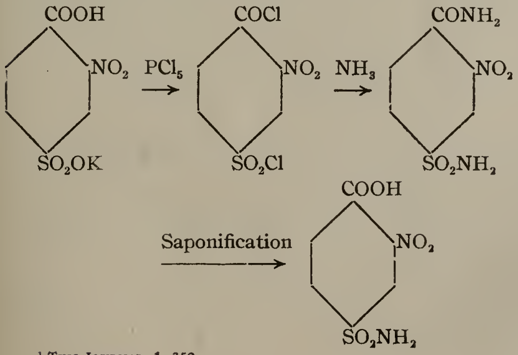
[1] Ber. d. chem. Ges., **21**, 3220.

[2] THIS JOURNAL, **1**, 352.

I thought now that by oxidizing the methyl group to carboxyl I might obtain *o*-nitro-*p*-sulphamidobenzoic acid. Two and sixteen-hundredths grams of the *p*-sulphamido-*o*-nitrotoluene were treated with 0.8 gram of potassium hydroxide to get the amide into solution, then 3.16 grams of potassium permanganate were added in small portions at a time on the water bath. There was a noticeable evolution of ammonia during the oxidation. The oxides of manganese were filtered off and the clear solution acidified with hydrochloric acid but no precipitate was formed. Barium chloride was now added to the solution and 0.18 gram of barium sulphate was obtained, showing that part of the sulphur of the amide had been oxidized to sulphuric acid. The solution was concentrated to crystallization and 1.2 grams of the original *p*-sulphamido-*o*-nitrotoluene were obtained unchanged.

Having been unable to obtain *p*-sulphamido-*o*-nitrobenzoic acid by this method, I next made *p*-sulpho-*o*-nitrobenzoic acid from calcium *o*-nitrotoluene-*p*-sulphonate, according to Hart's directions.[1]

From the acid potassium salt I hoped to obtain *o*-nitro-*p*-sulphamidobenzoic acid as follows:



[1] This Journal, **1**, 352.

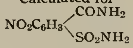
I treated 68 grams of the acid potassium salt with 125 grams of phosphorus pentachloride and heated the mixture on the water bath until the whole mass liquefied. After washing about five times with 150 cc. portions of ice water, I obtained the dichloride as a thick yellow oil. This yellow oil was at first treated with concentrated ammonium hydroxide directly in order to prepare the diamide, but the reaction was so violent that I had to use dilute ammonium hydroxide. After evaporating off the excess of ammonia and heating up with charcoal, the diamide came out in fine, silky needles, which, when recrystallized, melted at 226°.

Analysis:

0.404 gram gave 0.3777 gram $BaSO_4$ (Liebig).

0.4422 gram gave 0.4276 gram $BaSO_4$ (Liebig).

0.3936 gram gave with NaOH ammonia equivalent to 7.7 cc. 0.1 N acid.

	Calculated for  $NO_2C_6H_3\begin{smallmatrix}CONH_2\\SO_2NH_2\end{smallmatrix}$	Found	
		I	II
S	13.00	12.84	13.28
$^1/_3$ N	5.71	2.78	...

From the above analysis for nitrogen, it seems that the nitro group in the ortho position has prevented the saponification of the carbamido group. Five and seven-tenths grams of the diamide were now boiled with an excess of caustic soda for two days, after which the solution was neutralized with hydrochloric acid and digested with charcoal to take out the red color, which is always formed when the diamide is made alkaline. On concentrating the solution, nothing came down until it had gone nearly to dryness, when sodium chloride crystallized out. Nothing else could be isolated from the solution. From the above experiments it is evident that 1-carbamido-2-nitro-4-sulphamidobenzene cannot be saponified by the usual methods, viz., boiling with alkalies, so the method of Bouveault,[1] as modified by Gattermann,[2] was tried out as follows:

Twenty grams of the diamide were dissolved in a boiling solution of 50 per cent. sulphuric acid and cooled to about 60°. Then 20 grams of sodium nitrite in 30 cc. of water were gradually led into the solution of the diamide from the bottom by means of a pipette. The solution turned somewhat milky when nearly all the nitrite had been added, but on boiling it cleared up again with the evolution of a gas.

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[1] Bull. soc. chim., **9**, 372.

[2] Ber. d. chem. Ges., **32**, 1118.

The solution was now concentrated and extracted three times with ether. On evaporating off the ether, a thick oily liquid was left which could not be made to crystallize. This oily extract was dissolved in water and neutralized with barium hydroxide, when a thick precipitate came down. This precipitate was almost completely soluble in hot water, only a small amount remaining undissolved. The barium salt came down from water as an amorphous powder, which I was unable to get out pure enough for analysis because of lack of time.

It is very probable, though, that both the carbamido and sulphamido groups have been decomposed by the nitrous acid, giving *o*-nitro-*p*-sulphobenzoic acid, and the salt obtained by neutralizing the ether extract with barium hydroxide is nothing more than barium *o*-nitro-*p*-sulphobenzoate. The aqueous solution was concentrated to a very small volume, when sodium sulphate crystallized out.

JOHNS HOPKINS UNIV.

VELOCITY COEFFICIENTS OF THE REACTION BETWEEN ETHYL IODIDE AND SILVER NITRATE IN ETHYL AND METHYL ALCOHOLS AND MIXTURES OF THESE SOLVENTS

BY J. N. PEARCE AND OTIS M. WEIGLE

Burke and Donnan[1] made an extensive study of a number of reactions involving alkyl iodides and silver nitrate in ethyl alcohol. They found the reaction to be "pseudobimolecular" in character, i. e., the velocity coefficients of the simple bimolecular equation vary (increase) considerably with the initial concentration of the reacting substances, although they remain fairly constant during the course of any particular reaction.

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[1] J. Chem. Soc., **85**, 555 (1904).

They found also that the velocity coefficient, *k*, increases with increasing initial concentration of silver nitrate when the nitrate and the iodide are present in equivalent proportions. Using the same initial concentrations of silver nitrate and varying the proportions of ethyl iodide, the constants, *k*, are found to decrease with increasing concentration of ethyl iodide. When the iodide is kept constant, the velocity coefficients increase with increasing initial concentrations of silver nitrate. They were not able to explain the variation in the values of *k*.

The velocity coefficients in ethyl alcohol, using 0.025 N equivalent solutions of silver nitrate and various alkyl iodides, were found to decrease in the following order: isopropyl, ethyl, *n*-propyl, methyl, *n*-butyl, isoamyl and isobutyl iodide, respectively.

The velocity coefficients of four of the iodides, methyl, ethyl, *n*-propyl and *n*-butyl, were likewise determined in methyl alcohol, using 0.025 N equivalents of iodide and silver nitrate.

In every case the velocity coefficients were greater than in ethyl alcohol, the ratio $k_{\mathrm{MeOH}}/k_{\mathrm{EtOH}}$ being approximately equal to 2.

An addition of water to the extent of ten per cent. produced only a slight increase in the value of *k*. The addition of benzene (10 per cent.), a nondissociating solvent, gave a slightly lower value for *k*.

In a second paper, Burke and Donnan[1] give the results of further study of the reaction of ethyl iodide and silver nitrate in ethyl alcohol. Their purpose was to study the effect of the reaction products upon the velocity coefficients, and to determine which is the disturbing factor. Experiments proved that this disturbance is not due to ethyl nitrate, or ether, while nitric acid slightly retards the speed. The velocity coefficients are increased by the addition of both calcium and ammonium nitrates. A series of experiments on the amount and rate of formation of nitric acid during the reaction in ethyl alcohol showed that the nitric acid formed is always a constant percentage (about 70 per cent.) of the amount of silver nitrate which has reacted, and the amount formed is independent of the initial concentrations of the reactants. More acid seems to be formed in mixtures of alcohol and water than in either pure solvent. The velocity coefficient curves for ethyl and methyl iodides in the aqueous alcoholic mixtures show a pronounced maximum near the alcohol end of the curve.

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[1] Z. physik. Chem., **69**, 148 (1909).

They offer as a tentative suggestion for the variation in the velocity coefficients with change in initial concentrations that "it is the undissociated silver nitrate which reacts and that the decrease in the bimolecular velocity coefficients which might be expected therefrom is compensated by the accelerating action of one of the reaction products." They were, however, unable to determine which of the products is the disturbing factor.

Donnan and Potts[1] made an attempt to determine whether the peculiar behavior already noted is due to the presence of the NO_3 group. They substituted silver lactate for silver nitrate in 60 per cent. alcohol-water solutions. Two series, with different equivalent concentrations of the reactants, were studied. The results showed that the disturbing factor in this case is absent. The ratio of the lactic acid formed to that of the silver lactate used up was the same as for nitric acid and silver nitrate, viz., approximately 70 per cent.

Since free acid is one of the main products when solvents containing a hydroxyl group are used, they decided to carry out the experiments with ethyl iodide and silver nitrate in acetonitrile. No acid, other than a slight trace, possibly due to impurities, was found. The experimental results resembled those obtained when alcohol was used as solvent. The simple bimolecular equation holds for all concentrations studied except the 0.1 N, but the velocity coefficients vary with the initial concentrations of the reacting substances. This would show then that the variation is not dependent upon the formation of acid.

Euler[2] studied the reaction between chloroacetic acid and

[1] J. Chem. Soc., **97**, 1882 (1910).

[2] Ber. d. chem. Ges., **39**, 2726 (1906).

silver nitrate in water and in 45 per cent. alcohol-water mixtures. The reaction speed in 0.25 N equivalent solutions was decreased 100 per cent. in the presence of 0.5 N nitric acid.

Senter[1] investigated the reactions between silver nitrate and bromoacetic, α-bromopropionic, α-bromobutyric acids and their sodium salts. Traces of silver bromide added to the reacting mixtures were found to increase the initial velocity coefficients three to six times. The same was found to be true when traces of silver iodide were added to reaction mixtures of methyl iodide and silver nitrate in aqueous solutions. In these experiments the addition of nitric acid shows considerable retarding effect. Benzenesulphonic acid was found to have a still greater retarding effect than nitric acid.

Senter suggests the catalytic action of the silver halides as being the possible cause of the kinetic disturbances observed in reactions in alcoholic solvents.

No measurements of the velocity coefficients of the reactions in the mixed alcohols have been made and very little done with silver nitrate and ethyl iodide in methyl alcohol as solvent. It was thought some interesting facts might be brought to light through a systematic study of the reactions of silver nitrate and ethyl iodide in methyl alcohol, ethyl alcohol, and their binary mixtures.

With this idea in view, these reactions were carried out in pure ethyl alcohol, 75, 50 and 25 per cent. mixtures with methyl alcohol, and pure methyl alcohol.

Materials and Solutions

Ethyl Alcohol.—Ethyl alcohol, after standing for several months over two changes of fresh quicklime, was fractionated and kept over anhydrous copper sulphate until ready for use. It was then fractionated, refluxed with about 30 grams metallic calcium per liter for several hours, fractionated, and immediately refluxed with fused silver nitrate for two hours, and fractionated into dry glass-stoppered bottles. A Glinsky distilling tube and soda-lime or calcium chloride guard tubes were used. Alcohol thus prepared gave a conductivity of 2.4×10^{-7} at

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[1] J. Chem. Soc., **97**, 346 (1910).

25° C., measured by the Kohlrausch method, with bridge, induction coil and telephone receiver. The Wheatstone bridge wire was calibrated by the method of Strouhal and Barus. The Arrhenius cell, as improved by Jones and Bingham, was used.

Methyl Alcohol.—Kahlbaum's best grade of methyl alcohol was further purified in the same manner as the ethyl alcohol except that the copper sulphate treatment was omitted. The conductivity at 25° C. was found to be 0.8×10^{-6}.

The mixtures of the alcohols were made up by weight, accurate to one-tenth gram per liter.

Silver Nitrate.—Merck's chemically pure silver nitrate was twice recrystallized from a saturated solution in conductivity water by quickly cooling from 60° to 20°. The product was washed with conductivity water, filtered as dry as possible on a Büchner funnel, dried in a toluene bath at 109° for several hours, and cooled in a desiccator, the work being done either at night or in the dark. Several unsatisfactory methods were previously tried, but this gave a product in small dry crystals, showing no sign of coloring.

Ethyl Iodide.—Kahlbaum's best grade of ethyl iodide was washed with dilute sodium hydroxide and water, dried over calcium chloride for two weeks, decanted, and fractionated. This, after nearly eleven months, has shown no tint of color.

Sodium Chloride.—This salt was precipitated by passing pure hydrogen chloride gas into a saturated solution of Merck's guaranteed chemically pure sodium chloride in conductivity water. The fine precipitate was filtered and washed on a Büchner funnel and dried in an electric oven at 110°. The portion used was heated, short of fusion, in a platinum crucible.

Ammonium Sulphocyanate.—Kahlbaum's best grade of good clear crystals was used.

Nitric Acid.—The best obtainable nitric acid, specific gravity 1.42, and free from chlorides, iodides and lower oxides of nitrogen, was kept in the dark in small bottles filled to the neck. Five cc. were used in each titration.

Iron Alum.—Five cc. of a saturated solution, made from good clear crystals, were used in each titration.

Water.—The water was purified by the method of Jones and Mackay:[1] ordinary distilled water was distilled from a large Jena flask containing a small amount of potassium bichromate and sulphuric acid. This was then doubly distilled from a similar flask and solution through a retort containing barium hydroxide and condensed through a block-tin tubing. This water was used in making up all aqueous solutions.

Solutions.—All solutions were made up to volume at 25°. Alcoholic solutions of silver nitrate and ethyl iodide were prepared seven to twenty hours before using, and of such a strength that when equal volumes of the two were mixed the normality desired was obtained. In all titrations 0.025 N silver nitrate and ammonium sulphocyanate solutions were used. The silver nitrate solution was made up by weight and checked against a standard sodium chloride solution by the Volhard method. The precipitate of silver chloride was filtered off before titrating with ammonium sulphocyanate. Since the results agreed very satisfactorily, the other solutions of silver nitrate were made up by weight.

Apparatus and Method

In general, the method used is similar to that followed by all experimenters in the measurement of velocity coefficients of chemical reactions.

All experiments were performed and solutions made up to volume in a constant temperature bath at 25° ± 0°.01. The motor-driven stirrer kept the water in the large granite tank in constant motion. The heat was supplied by means of a sixteen-candle power electric light bulb immersed in the bath and electrically controlled. The thermometer used was certified and graduated in tenths, such that it could easily be estimated to hundredths.

The bottles were suspended in the bath by means of a copper strip framework of clamps constructed for this purpose and which would accommodate twenty bottles at one time.

Every precaution was taken to keep the nitric acid, silver nitrate, ethyl iodide and solutions from the light. The reaction bottles and all solution bottles were thoroughly "seasoned," glass-stoppered, and well protected by sacks of heavy black cloth or paper.

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[1] THIS JOURNAL, **19**, 83 (1897).

Equal volumes of each solution were quickly poured together, stoppered and shaken thoroughly. Then ten cc. of the mixture, removed by a certified pipette previously warmed in the bath, were introduced into each of several small dry bottles which had been brought to temperature by suspension in the bath. The approximate instant of mixing was taken as the initial time. At previously decided instants, a known amount—always an excess—of 0.025 N ammonium sulphocyanate was quickly poured from an Erlenmeyer flask into the reacting solution to stop the reaction. This mixture was then poured back into the flask, the bottle rinsed three times with chlorine-free distilled water, the solution being diluted to over 100 cc. Five cc. each of a saturated solution of iron alum and of nitric acid were then added and the excess of ammonium sulphocyanate determined by titrating with 0.025 N silver nitrate. From this the amount of silver nitrate remaining in the solution at the instant of stopping the reaction was easily obtained.

One minute is taken as the unit of time. The unit of volume is one cc. The unit of concentration for silver nitrate is the amount of silver nitrate in one cc. of 0.025 N solution; e. g., the concentration of ten cc. of 0.05 N silver nitrate solution is twenty. The concentration of ethyl iodide is expressed in equivalent terms. Unless otherwise stated, all data are the average of duplicate experiments made the same day.

EXPERIMENTAL

Where the reacting substances are present in equivalent amounts, the velocity coefficients, k, are calculated according to the usual bimolecular reaction formula:

$$k = \frac{1}{t} \cdot \frac{x}{A(A - x)}$$

where x is the portion of the silver nitrate transformed in the time t and A is taken as its initial concentration.

In the case of all nonequivalent solutions the following form of the bimolecular equation was used:

$$k = \frac{1}{(A - B)t} \ln \frac{(A - x)B}{(B - x)A}$$

where the characters have the usual meaning.

Table I gives the results of duplicate experiments carried out in each of the five solvents, with equivalent solutions. For any particular reaction, the velocity coefficients show a fairly constant value. However, there is an unmistakable tendency to decrease, especially noticeable as the proportion of methyl alcohol increases, and this decrease is very much greater during the first part of the reaction. On the other hand, the velocity coefficients become larger as the proportion of methyl alcohol increases.

This is strikingly different from results obtained by Burke and Donnan[1] with mixtures of ethyl alcohol and water in which they found a maximum near the alcohol end of the velocity coefficient—solvent curve. It is doubtful if one is justified in considering the mean values of these velocity coefficients, but they will be used to bring out more clearly some general relations.

A variation from the law of averages is shown by a slight sagging of the curve when the mean constants for any one series are plotted against solvents.

By plotting the coefficients for each solvent in a series against time as abscissas, it will be seen that curves for the mixed solvents are drawn towards that in pure ethyl alcohol, thus showing the dominating influence of the latter solvent.

Table II shows the results of a series of experiments similar to those of Table I except that nonequivalent solutions were used, and the same general relations apply here. A comparison of these tables shows that with the same initial concentration of silver nitrate, the velocity coefficients increase as the initial concentration of the ethyl iodide decreases.

A much greater difference may be observed in the values of

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[1] *Loc. cit.*

Table I.—Velocity Coefficients. 0.025 N $AgNO_3$ and 0.025 N C_2H_5I in Alcohols as Solvents

100 per cent. ethyl alcohol			75 per cent. ethyl alcohol 25 per cent. methyl alcohol			50 per cent. ethyl alcohol 50 per cent. methyl alcohol			25 per cent. ethyl alcohol 75 per cent. methyl alcohol			100 per cent. methyl alcohol		
t	*c*	*k*	*t*	*c*	*k*	*t*	*c*	*k*	*t*	*c*	*k*	*t*	*c*	*k*
0	10.0	....	0	10.0	.....	0	10.0	.....	0	10.0	.....	0	10.0	.....
9	7.495	0.00371	5	8.12	0.00463	5	7.77	0.00574	5	7.49	0.00670	5.1	6.96	0.00856
18	6.055	0.00367	10	6.995	0.00430	10	6.67	0.00499	10	6.15	0.00626	10	5.535	0.00807
30	4.97	0.00337	15	6.185	0.00411	15	5.73	0.00497	15	5.145	0.00629	15	4.615	0.00778
50	3.785	0.00328	25	4.96	0.00406	25	4.63	0.00468	25	4.155	0.00563	28	3.385	0.00698
75	2.85	0.00334	40	3.96	0.00381	40	3.64	0.00437	40	3.205	0.00530	51	2.23	0.00683
100	2.12	0.00338	55	3.26	0.00376	55	2.965	0.00431	55	2.56	0.00528	70	1.775	0.00662
			75	2.69	0.00362	75	2.33	0.00438	75	2.08	0.00508			
			100	2.305	0.00334	100	1.895	0.00427	100	1.62	0.00517			

Table II.—Velocity Coefficients. 0.025 N $AgNO_3$ and 0.0125 N C_2H_5I in Alcohols as Solvents

100 per cent. ethyl alcohol			75 per cent. ethyl alcohol 25 per cent. methyl alcohol			50 per cent. ethyl alcohol 50 per cent. methyl alcohol			25 per cent. ethyl alcohol 75 per cent. methyl alcohol			100 per cent. methyl alcohol		
t	*c*	*k*	*t*	*c*	*k*	*t*	*c*	*k*	*t*	*c*	*k*	*t*	*c*	*k*
0	10.0	.....	0	10.0	.....	0	10.00	.....	0	10.0	.....	0	10.0	.....
10	8.445	0.00407	5	8.90	0.00528	5	8.78	0.00598	5	8.46	0.00804	5	8.345	0.00884
21	7.29	0.00443	10.5	8.145	0.00492	10.5	8.07	0.00521	10.5	7.59	0.00728	10	7.355	0.00891
36	6.875	0.00337	15	7.70	0.00473	15	7.43	0.00566	15	7.03	0.00732	18	6.51	0.00853
55	6.045	0.00386	20	7.32	0.00456	20	7.055	0.00540	20	6.63	0.00710	25	6.073	0.00831
75	5.71	0.00371	26	6.94	0.00447	26	6.645	0.00541	26	6.30	0.00681	32	5.82	0.00792
130	5.285	0.00343	33	6.65	0.00425	33	6.285	0.00542	33	6.005	0.00666	35	5.70	0.00802
200	5.06	0.00374	40	6.295	0.00444	40	6.10	0.00510	40	5.83	0.00628	43	5.495	0.00797
			50	6.05	0.00423	50	5.84	0.00498	50	5.615	0.00607			

NOTE.—*c* = concentration of silver nitrate.

the velocity coefficients in Tables II and III than was just seen in a comparison of Tables I and II.

It will be noted that, other conditions being the same, a change in the initial concentration of the silver nitrate (Tables IV, VII, and VIII) produces a much greater change in the velocity coefficients than does a similar change in the initial concentration of the ethyl iodide (Tables IV, V, VI).

A comparison of Tables VI and VIII, using the most concentrated solution of the silver nitrate with the weakest concentration of the ethyl iodide, and vice versa, shows that the reaction in the former proceeds much more rapidly than that in the latter, the same amount of silver nitrate being used up in one-third to one-fourth the time required by the corresponding reactions in Table VIII.

According to the law of mass action, the velocity of a bimolecular reaction should be directly proportional to the product of the reacting masses. That other influences than those due to concentration of the reacting substances are at work may be seen by a comparison of Tables VI and VIII. The values of k representing the proportionality between velocities and the products of the active masses vary widely for each solvent.

In order to make certain that no changes were taking place in the apparatus, solutions, or methods during the investigation, a check experiment was carried out with the results as shown in Table X. It is clearly seen that after nearly three months these data could be reproduced quite accurately.

A tabulation of the mean velocity coefficients, Table XI, gives a general survey of the work covered, and may serve to bring out more clearly some of the points already noted. A natural order of tabulation readily shows the increase of the velocity coefficients with increasing initial concentration of silver nitrate. Taking any given concentration of ethyl iodide, e. g., 0.0125 N, the change in the velocity coefficients is considerable. This change is greater as the methyl alcohol increases. Again, consider a series in which the concentration of silver nitrate is the same, e. g., 0.0125 N. The mean constants decrease with increase in the initial concentration

Table III.—Velocity Coefficients. 0.0125 N $AgNO_3$ and 0.0125 N C_2H_5I in Alcohols as Solvents

100 per cent. ethyl alcohol			75 per cent. ethyl alcohol 25 per cent. methyl alcohol			50 per cent. ethyl alcohol 50 per cent. methyl alcohol			25 per cent. ethyl alcohol 75 per cent. methyl alcohol			100 per cent. methyl alcohol		
t	*c*	*k*	*t*	*c*	*k*	*t*	*c*	*k*	*t*	*c*	*k*	*t*	*c*	*k*
0	5.0	.....	0	5.0	.....	0	5.0	.....	0	5.0	.....	0	5.0	.....
11	4.06	0.00421	10	4.46	0.00242	10	4.205	0.00378	10	4.125	0.00424	5	4.31	0.00640
21	3.82	0.00294	23	3.88	0.00251	22	3.675	0.00328	23	3.495	0.00374	10	3.90	0.00564
45	3.25	0.00243	31	3.61	0.00248	31.1	3.30	0.00531	31	3.12	0.00389	25	2.965	0.00549
70	2.755	0.00237	45	5.26	0.00237	45	2.85	0.00335	45	2.695	0.00380	40	2.42	0.00533
110	2.06	0.00260	65.5	2.81	0.00258	65.5	2.39	0.00333	65.5	2.235	0.00378	60	1.945	0.00524
135	1.695	0.00290	85	2.55	0.00229	85	2.14	0.00315	85	1.95	0.00368	90	1.49	0.00524
170	1.55	0.00262	110	2.20	0.00251	110	1.855	0.00314	110	1.66	0.00366	120	1.16	0.00552
			130	2.00	0.00231	130	1.64	0.00315	150	1.50	0.00359			

Table IV.—Velocity Coefficients. 0.05 N $AgNO_3$ and 0.05 N C_2H_5I

100 per cent. ethyl alcohol			50 per cent. ethyl alcohol 50 per cent. methyl alcohol			100 per cent. methyl alcohol		
t	*c*	*k*	*t*	*c*	*k*	*t*	*c*	*k*
0	20.0	.....	0	20.0	.....	0	20.0	.....
9	9.29	0.00640	4	12.125	0.00812	4	10.36	0.01163
29	4.72	0.00558	7	9.41	0.00804	8	7.625	0.01014
50	3.375	0.00493	10	8.085	0.00737	12	5.975	0.00978
70	2.485	0.00503	15	6.49	0.00694	18	4.56	0.00941
95	1.995	0.00475	21	5.285	0.00663	20	4.41	0.00884
			25	4.86	0.00623	23	4.17	0.00825
			40	3.63	0.00564	30	3.435	0.00804
			50	3.075	0.00550	43	2.855	0.00698

Table V.—Velocity Coefficients. 0.05 N $AgNO_3$ and 0.025 N C_2H_5I

100 per cent. ethyl alcohol			50 per cent. ethyl alcohol 50 per cent. methyl alcohol			100 per cent. methyl alcohol		
t	*c*	*k*	*t*	*c*	*k*	*t*	*c*	*k*
0	20.0	.....	0	20.0	.....	0	20.00	.....
10.75	13.13	0.00689	5	14.38	0.00991	7	12.21	0.01452
20	11.585	0.00648	7	13.485	0.00943	10	11.38	0.01417
39	10.51	0.00598	10	12.505	0.00915	13	10.92	0.01370
55	10.17	0.00618	13	11.80	0.00913	16	10.645	0.01319
			18	11.10	0.00899	20	10.525	0.01153
			26	10.555	0.00866			

Table VI.—Velocity Coefficients. 0.05 N $AgNO_3$ and 0.0125 N C_2H_5I

100 per cent. ethyl alcohol			50 per cent. ethyl alcohol 50 per cent. methyl alcohol			100 per cent. methyl alcohol		
t	*c*	*k*	*t*	*c*	*k*	*t*	*c*	*k*
0	20.0	.....	0	20.0	.....	0	20.0	.....
5.04	17.695	0.00655	2	18.18	0.01190	2	17.60	0.01754
12	16.335	0.00621	4	17.25	0.01084	4	16.445	0.01743
24	15.555	0.00541	6	16.56	0.01084	6	15.915	0.01633
30	15.31	0.00558	8	16.17	0.01033	8	15.595	0.01567
36	15.175	0.00570	10	15.83	0.01041	10	15.36	0.01578
			14	15.43	0.01045	14	15.17	0.01479

Table VII.—Velocity Coefficients. $0.025\ N\ AgNO_3$ *and* $0.05\ N\ C_2H_5I$

100 per cent. ethyl alcohol			50 per cent. ethyl alcohol 50 per cent. methyl alcohol			100 per cent. methyl alcohol		
t	*c*	*k*	*t*	*c*	*k*	*t*	*c*	*k*
0	10.0	.....	0	10.0	.....	0	10.0	.....
10.07	5.755	0.00312	5	6.50	0.00477	6.35	4.75	0.00695
23	3.135	0.00322	9	4.88	0.00469	9	3.905	0.00641
34	2.305	0.00289	13	3.92	0.00442	13.16	2.91	0.00605
45	1.70	0.00275	18	2.94	0.00438	19	1.75	0.00637
60	1.215	0.00255	23	2.51	0.00397	23.5	1.445	0.00586
90.04	0.585	0.00245	30	1.905	0.00380	28	1.17	0.00558
100	0.56	0.00224	40	1.245	0.00377	35	0.93	0.00506
			55	0.765	0.00355	45.5	0.585	0.00484

Table VIII.—Velocity Coefficients. $0.0125\ N\ AgNO_3$ *and* $0.05\ N\ C_2H_5I$

100 per cent. ethyl alcohol			50 per cent. ethyl alcohol 50 per cent. methyl alcohol			100 per cent. methyl alcohol		
t	*c*	*k*	*t*	*c*	*k*	*t*	*c*	*k*
0	5.0	.....	0	5.0	.....	0	5.0	.....
4	4.05	0.00270	4	3.92	0.00313	4	3.57	0.00438
7	3.64	0.00325	7	3.395	0.00289	8	2.645	0.00426
10	3.14	0.00254	10	2.795	0.00310	13	1.85	0.00422
17.14	2.34	0.00240	17	1.975	0.00300	16	1.505	0.00420
28	1.585	0.00229	23	1.52	0.00290	20.5	1.20	0.00396
35.5	1.26	0.00220	30	1.09	0.00290	24	0.91	0.00410
63	0.42	0.00235	37	0.835	0.00280	28	0.78	0.00386
			45	0.59	0.00280	32	0.615	0.00385

Table IX.—Velocity Coefficients. $0.0125\ N\ AgNO_3$ *and* $0.025\ N\ C_2H_5I$

100 per cent. ethyl alcohol			50 per cent. ethyl alcohol 50 per cent. methyl alcohol			100 per cent. methyl alcohol		
t	*c*	*k*	*t*	*c*	*k*	*t*	*c*	*k*
0	5.0	.....	0	5.0	.....	0	5.0	....
10	3.865	0.00274	5	4.17	0.00380	5	4.015	0.00463
19.08	3.175	0.00265	10.5	3.72	0.00302	10	3.28	0.00466
30	2.63	0.00248	15	3.27	0.00313	15	2.705	0.00472
45	1.88	0.00268	25	2.55	0.00314	25	1.98	0.00453
60	1.56	0.00248	35	2.08	0.00304	33	1.51	0.00465
80	1.05	0.00264	45	1.67	0.00307	42	1.265	0.00432
130	0.425	0.00285	60	1.30	0.00295	51	0.98	0.00437
160	0.225	0.00306	80	0.89	0.00299	60	0.77	0.00440

Table X.—Velocity Coefficients. $0.025\ N\ AgNO_3$ *and* $0.025\ N\ C_2H_5I$

Solvent: Ethyl alcohol

Average of two experiments January 15			A single experiment (check) April 12		
t	*c*	*k*	*t*	*c*	*k*
0	10.0	.....	0	10.0	.....
9	7.495	0.00371	9	7.48	0.00374
18	6.055	0.00362	18	6.04	0.00364
30	4.97	0.00357	30	4.95	0.00340
50	3.785	0.00328	50	3.80	0.00326
75	2.85	0.00334	75	2.87	0.00331
110	2.12	0.00338	110	2.16	0.00330

Table XI.—Mean Velocity Coefficients of the Reactions between Silver Nitrate and Ethyl Iodide in Alcohols

Silver nitrate	Ethyl iodide	C_2H_5OH	75 per cent. 25 per cent.	50 per cent. 50 per cent.	25 per cent. 75 per cent.	CH_3OH
0.0125 N	0.05 N	0.00239		0.00294		0.00410
0.0125 N	0.025 N	0.00270		0.00314		0.00454
0.0125 N	0.0125 N	0.00286	0.00239	0.00380	0.00380	0.00557
0.025 N	0.05 N	0.00274		0.00417		0.00589
0.025 N	0.025 N	0.00345	0.00396	0.00471	0.00571	0.00747
0.025 N	0.0125 N	0.00380	0.00465	0.00540	0.00695	0.00836
0.05 N	0.05 N	0.00534		0.00681		0.00913
0.05 N	0.025 N	0.00638		0.00921		0.01342
0.05 N	0.0125 N	0.00589		0.01080		0.01625

of ethyl iodide, but the change is much less than in the former case. These facts, already observed by Burke and Donnan[1] in the use of ethyl alcohol as solvent, are now applicable to these reactions carried out in methyl alcohol and in their binary mixtures.

SUMMARY

The velocity coefficients of the reactions of thirty-three of the forty-five possible combinations of concentrations, using 0.05, 0.025, and 0.0125 N solutions of silver nitrate and ethyl iodide in ethyl alcohol, methyl alcohol, and three of their binary mixtures, were obtained.

The velocity coefficients of any particular reaction, calculated by the usual bimolecular equation, show in most cases a fairly constant value. However, they show a decrease as the reaction proceeds and this decrease is more marked in the methyl alcohol and in the mixtures than in the pure ethyl alcohol as solvent.

Time-constant curves for any one concentration in the solvents used show a displacement toward the ethyl alcoholic solvent, thus indicating that this solvent has the greater influence on the reaction.

This is also shown by plotting the mean velocity coefficients against solvents. A slight sagging of the curve shows that the velocity coefficients for the mixtures are a trifle smaller than would be expected from the law of averages.

For the concentrations considered, the coefficients are always greater in methyl alcohol than in ethyl alcohol as solvent.

For any given initial concentration of ethyl iodide in the solvents used, the bimolecular velocity coefficients increase as the initial concentration of the silver nitrate increases. For a given initial concentration of silver nitrate, they decrease as the initial concentration of the ethyl iodide increases, but the change in the coefficients is very much less in the latter case.

The difference in the effects of the two reacting constituents, which is apparently due to the presence of an excess or large

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[1] *Loc. cit.*

amount of silver nitrate, increases as the proportion of methyl alcohol in the solvent increases.

Physical Chemical Laboratory
State University of Iowa
May 25, 1912

REVIEWS

A Dictionary of Applied Chemistry. By Sir Edward Thorpe, C.B., LL.D., F.R.S., Professor of General Chemistry and Director of the Chemical Laboratories of the Imperial College of Science and Technology, South Kensington, London, assisted by Eminent Contributors. Revised and enlarged edition in five volumes. Vol. II, Chi-Gou. With illustrations. London, New York, Bombay and Calcutta: Longmans, Green & Co. 1912. pp. viii + 786. Price, $13.50.

The first volume of this new edition has been recently reviewed in these columns, and it is a pleasure to find the second volume appearing so promptly, thus supporting the promise of the early prospectus that the entire work will be complete in two years. As in the first volume, among the names of the contributors are found many who are recognized as world-wide authorities in their respective subjects.

Comparing the alphabetical range of this volume with the same field covered in the old edition, it appears that about sixty-five new articles have been introduced, of which the following are some of the more important: Chromophores and Chromogens; Colloids; Corrosion of Iron and Steel; Cryoscopy; Denaturants; Desiccation and Drying; Diazo Compounds; Diffusion; Egg; Emulsin; Esterification; Fertilizers; Flame; Flash Lights; and Flavanthrene. In these articles, with one or two exceptions, numerous references to the original literature bring the material up to about the end of 1910. The chapter on Colloids is an excellent brief summary of the subject according to the more recent views. Considering the importance of the subject, and the large amount of investigation which has been carried on with reference to the Corrosion of Iron and Steel by Dunstan, Friend, Moody, Cribb, Traube, Whitney, Cushman, Walker, and others, the omission of all references to original papers in this article is to be regretted. Under Esterification, we find a good theoretical consideration of the reaction between an acid and an alcohol. Flame is discussed from the view point of utility, rather than a detailed consideration of the complex chemistry involved in most cases of combustion. Space does not permit of a detailed consideration of each of these new articles, but in each is found a concise and readable treatment of the subject in hand. Besides these new topics introduced, a large amount of new matter has been incorporated in some of the subjects transferred from the old edition; in many cases these have been entirely rewritten, as in the case of Chlorine, Cyanides, Diamond, Disinfectants, Dyeing, Electroplating, Explosives, Fermentation, Formaldehyde, and the excellent discussion of Fuel. Under Chlorine is a very good résumé of the present state of this industry, including the more recent developments in the electrolytic methods, with diagrams of the principal commercial cells. But it is somewhat surprising to read in the opening sentence under Potassium Chlorate, "This salt is always manufactured by the process first indicated by Liebig; . . . ." The manufacture by electrolysis is, however, given about half a page at the end of the article, as compared with the nearly three and a half pages devoted to the old lime process. Under hydrochloric acid manufacture no mention is made of the process of Askenazy, or of Masson, by the action of chlorine and steam on sulphuric acid, nor of Roberts' process for direct combination of chlorine and hydrogen, which has been used at Niagara Falls. Since the first edition appeared, the Cyanides have attained great commercial importance, and under this head is found a good digest of the various methods of production. The chapter on Dyeing has been remodeled and the various theories of the process are summed up with the conclusion, "that the attempt to cover all dyeing phenomena by any one simple explanation must fail, and that many factors are concerned, the relative importance of which varies in different cases." For practical purposes the dyestuffs are classified in eight groups: Mordant dyes, acid-mordant dyes, acid dyes, direct dyes, basic dyes, sulphide dyes, vat dyes, and ingrain colors. With each class is given a short outline of the method of dyeing on the different fibers. In the topic "Explosives" is found an extended and up-to-date treatment of the properties, manufacture and testing of these various substances. The section on Fuels includes a discussion of the calorific value and methods for its determination; the composition, properties and mode of occurrence of the various solid, liquid and gaseous fuels; and numerous illustrations of industrial gas producers and methods of purifying and cooling the gas. The general arrangement and make-up of the book is concordant with Vol. I[1] and the same care in editing and publishing is obvious.

F. H. Thorp

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[1] This Journal, **48**, 191.

DIE FABRIKATIONEN VON BITTERSALZ UND CHLORMAGNESIUM als Nebenbetriebe der Chlorkalium- und Kaliumsulfat-Fabrikation. Von CHEMIKER DR. PHIL. AUGUST BERGE, früher Betriebsführer der chemischen Fabriken auf "Mecklenburgische Kalisalzwerke Jessenitz." Mit 15 Abbildungen im Text. Monographien über chemisch-technische Fabrikations-Methoden. Band XXVIII. Halle a. S.: Verlag von Wilhelm Knapp. 1912. pp. vi + 61. Price, M. 3.00.

As in the case of each of the previously issued monographs of this series, this booklet is written by an expert, having extensive personal knowledge of his subject. Beginning with a short historical sketch of the development of the Potash Industries at Stassfurt, the author passes to a consideration of the various by-products from potassium chloride manufacture. About one-third of the work is devoted to the details of Epsom salt making from kieserite. Diagrams of the apparatus for dissolving, clarifying, settling, crystallizing and drying the product are included.

The recovery of magnesium chloride, its purification and uses, comprise the remainder of the book. For those having direct interest in these industries the little work contains many valuable hints.

F. H. THORP

ALLEN'S COMMERCIAL ORGANIC ANALYSIS. Volume VI. By the Editors and the Following Contributors: W. H. GLOVER, THOMAS A. HENRY, FRANK O. TAYLOR, R. W. TONKIN, FRANCIS H. CARR, SAMUEL S. SADTLER, J. J. FOX, CHARLES E. VANDERKLEED, OLIVER CHICK, EDWARD HORTON, P. J. SAGEMAN, R. WHYMPER. Fourth edition, entirely rewritten. Edited by W. A. DAVIS, B.Sc., A.C.G.I., and SAMUEL S. SADTLER, B.Sc. Philadelphia: P. Blakiston's Son & Co. 1912. pp. ix + 726. Price, $5.00.

The present volume of Allen corresponds to Part II of Volume III, published twenty years ago, and comprises about 150 pages of additional matter. The divisions of the book and the authors are: Amines and Ammonium Bases (Davis); Aniline and its Allies (Sadtler); Naphthylamines, Pyridine, Quinoline and Acridine Bases (Glover); Vegetable Alkaloids (Henry); Volatile Vegetable Bases (Taylor); Nicotine and Tobacco (Tonkin); Aconite Alkaloids (Carr); Atropine and its Allies (Carr); Cocaine (Sadtler); Opium Alkaloids (Taylor); Strychnos Alkaloids (Vanderkleed); Cinchona Alkaloids (Chick); Berberine and its Associates (Horton); Caffeine, Tea and Coffee (Fox and Sageman); Cocoa and Chocolate (Whymper).

While the division of the work in this way has the advantage that the subject matter is presented authoritatively from various points of view, it has the disadvantage that it lacks a certain continuity of treatment as compared with the older volume, prepared under the direct supervision of Mr. Allen. This is unfortunate in that the proper correlation of the alkaloids is lost to a degree, and the general reader could well sacrifice some of the detailed descriptive matter for general methods of separation applicable in practical cases. The book is one for reference on special points rather than a laboratory companion for the busy chemist.

The chapters on the various alkaloids contain a wealth of information, well presented and accompanied by references to the journal literature. The chapter on nicotine and tobacco does not measure up to the standard of some of the others. The last two divisions on the book are treated more from a strictly analytical standpoint, the methods chosen following largely those of the American Official Chemists. Even so, some of the important work which has been done in the country in recent years has been overlooked. In the case of coffee, for instance, analyses of coffee beans made fifty years ago are quoted at length, while the complete analyses made by Lythgoe as associate referee for the A. O. A. C. are not mentioned. In the analyses of cocoa the extensive work done by Winton and his associates at the New Haven Experiment Station is entirely omitted. Dubois' older method for estimating sugars in milk chocolate is given at length, but his later modification, when the unsatisfactory polarization at 86° is obviated, is missing. The discussions and interpretations of analyses, on the other hand, are extremely valuable and make these two of the most helpful chapters in the book. The trained chemist will find in the whole book a great deal of information gathered within easy reach, although a more detailed index would render it more readily accessible. A. G. WOODMAN

MATERIALS FOR PERMANENT PAINTING. A Manual for Manufacturers, Art Dealers, Artists and Collectors. By MAXIMILIAN TOCH, Municipal Lecturer on Paints, Colors, etc., College of the City of New York, Director of the Chemical Laboratory of Toch Brothers. New York: D. Van Nostrand Co. 1911. pp. 208. Price, $2.00.

Contents: History of Painting; Pigments Used by the Ancients; Sinopia, the Search for the Master's Secret; Photo-Chemical Deterioration of Oil Paintings; Cause of the Cracking of Paintings and the Remedies; Canvas, Wood and Metal as Foundations; Preparation of Canvas in Commercial Practice; Renovation and Cleaning of Pictures; The School of Impressionism; Volatile Solvents; Picture Varnishes; Driers, Linseed Oil and Other Drying Oils; Classification of the Pigments and Their Description; The Permanent Colors; Pigments Dangerous to Health; Pigments Affected by Coal Smoke, etc.; Water in Tube Colors; Pigments which are Permanent, etc.; Pigments which Dry Slowly; The Failure of Sir J. Reynold's Paintings.

This little volume containing 190 pages, covering the subjects stated in the contents should be of much value to artists and decorators in supplying sound and accurate information pertaining to the art and craft of painting.

Many of the mysteries and some of the fallacies held regarding the work of the early masters are explained by the analyses made by the author of the pigments used in their paintings which have survived the effect of time.

The secret of the permanence of these masterpieces is due to the "survival of the fittest" and shows that permanent colors can be obtained now if the artist is willing to use only these pigments which are known to be lasting.

The chapters on deterioration and cracking of paintings, material and preparation of the foundation furnish a scientific explanation of many failures which can be prevented.

The chapter on "Renovation and Cleaning of Pictures" supplies the theoretical factors to be considered in this important phase of the art but can hardly supplement the knowledge and experience necessary to secure success.

Probably the most valuable information is contained in Chapter XIV, "Classification of the Pigments and Their Description" occupying about one-half of the volume.

In this chapter are listed practically all the artists' colors with a brief description of their origin, characteristics, methods of manufacture. This chapter can be studied to advantage by both the artist and the artisan as it shows a relatively few of the permanent earth pigments can be successfully used to produce practically all the colors required either in the studio or the shop.

It is instructive to note that while 94 pages are needed to list and describe these pigments, two pages only are required to list "The Permanent Colors."

The book is provided with an excellent index and the text and illustrations are such as to form an attractive volume.

S. S. Voorhees

Tests of the Absorptive and Permeable Properties of Portland Cement Mortars and Concretes, together with Tests of Damp-Proofing and Water-Proofing Compounds and Materials. By Rudolph J. Wig, Associate Engineer-Physicist, and P. H. Bates, Chemist, Bureau of Standards. Technologic Paper No. 3, Bureau of Standards. Washington: Government Printing Office. 1912. pp. 127.

At a time when manufacturers of water-proofing and damp-proofing compounds for use with Portland cement mortars are warning their competitors and prospective customers against the manufacture, purchase or use of similar compounds under penalty of prosecution for infringement, there is published by that department of the Government which is devoting its time to the examination and testing of structural materials a bulletin describing a series of tests which seem to indicate that these compounds have very little value for their advertised purpose. Representative samples of all classes of water-proofing and damp-proofing preparations were purchased on the open market and carefully planned and executed tests were made.

The results for absorption and permeability showed that the richness of the mixture and the ratio of coarse to fine material are the chief factors in the permeability which decreases with age and the flow of water, the decrease being less marked in lean specimens. It is concluded that with care in proportioning the aggregate, cements may be water-proofed without the addition of any of these "water-proofing" compounds. Where well graded sand is not obtainable, hydrated lime, clay or a larger proportion of cement may be substituted. The addition of small amounts of hydrated lime or clay does not affect the tensile or compressive stength. See *Chemical Abstracts* for more detailed description of results. More extensive tests are contemplated. C. N. WILEY

NOTIONS FONDAMENTALES D'ANALYSE QUALITATIVE. Par V. THOMAS, Professeur-adjoinct à la Faculté des Sciences de Clermont-Ferrand, et D. GAUTHIER, Chef des Travaux de Chimie à la Faculté des Sciences de Clermont-Ferrand. Paris: Gauthier-Villars. 1912. pp. viii + 326. Price, Fr. 10.

The first two of the three parts into which this work is divided constitute a short treatise on Inorganic Chemistry from the standpoint of Qualitative Analysis. Part I is devoted to a description of the apparatus and operations usually employed in both wet and dry methods. The construction and use of the microscope and spectroscope are carefully explained.

The second part consists of a fairly comprehensive treatment of the characteristic reactions and salts of the common base- and acid-forming elements. The acids are treated in groups and the means of identification of each pointed out. Oxalic, acetic and tartaric acids are omitted and no mention is made of cyanides or sulphocyanates.

In Part II the separation into groups and subsequent identification of the elements are dealt with. The various methods commonly employed within each group are given and the respective advantages and disadvantages pointed out. Appendix I contains notes on the reagents, Appendix II specific gravity tables, and Appendix III some reactions on the rarer elements.

The book differs materially from those published in this country in recent years in that it contains no analytical tables and no theory. As it is, according to the authors, primarily written for students it seems a questionable procedure to so completely separate theory and practise. Little is said with regard to the delicacy of the various tests given and the quantitative idea is almost entirely lacking.

With good laboratory notes the book should be valuable as an aid in developing independence on the part of the student. As a laboratory manual it is much too indefinite and it is difficult to see how the beginner would approach the subject using this book as a text. Notions Fondamentales is an excellent reference book in qualitative analysis and as such should prove a valuable addition to the chemical library.

ELWOOD B. SPEAR

DIE CHEMISCHEN GRUNDLEHREN NACH MENGE, MASS UND ZEIT. Von J. H. VAN'T HOFF. Mit 12 in den Text gedruckten Abbildungen und einem Vorwort von ERNST COHEN. Braunschweig: Druck und Verlag von Friedr. Vieweg und Sohn. 1912. pp. x + 91. Price, M. 4.00.

The examination of this little booklet leaves a feeling of sadness in the hearts of those who are more or less familiar with the contributions to science of this truly great man. This feeling is intensified in those who had the privilege of coming into personal contact with this modest, unselfish and genial nature. This is probably the last work from the pen of him who found chemistry essentially empirical, and who left it well advanced towards becoming a branch of exact science.

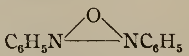
The really great and epoch-making developments in chemistry, as in every other branch of science, are due to a few—a very few—master minds. It must be stated that this is one of van't Hoff's lesser contributions to chemical science. As its title implies, it deals with conceptions which are essentially physical, yet physics and chemistry are, after all, only closely allied branches of the one great science of nature. H. C. J.

LABORATORY EXERCISES IN PHYSICAL CHEMISTRY. By J. N. PRING, D.Sc., Lecturer and Demonstrator in Electro-chemistry. Publications of the University of Manchester, Physical Series, No. II. Manchester: The University Press; New York: Longmans, Green & Co. pp. xii + 162. 1911. Price, $1.25.

The author of this little book states in his preface that it is "designed to meet the requirements of students who wish to follow a laboratory course dealing with some of the applications of physical chemistry." The list of experiments selected by Dr. Pring is quite different from that found in most physico-chemical laboratory manuals but with the growth of the science of physical chemistry in recent years it is no longer possible to include in a laboratory manual intended for the general student examples of every method used by the physical chemist. The manual is divided into three parts. In the first part seventeen exercises in general physico-chemical measurements, calorimetry and electrochemistry are given, the experiments on the charge and discharge of an accumulator being especially commendable. The second part is devoted to electrolytic preparations of such substances as aniline, azobenzene and potassium chlorate. Pyrometry is the subject treated in the third part of the book, brief but clear descriptions of thermo-electric, radiation and optical pyrometers being given, together with directions for the calibration and use of these instruments.

To include in a physico-chemical laboratory manual exercizes on electro-analysis and electro-synthesis seems somewhat inappropriate, but since laboratory manuals are prepared primarily to meet local conditions perhaps it is unfair to criticize the insertion of these topics.

Several errors in the text should be pointed out. On p. 59 we read, "Electrolyse with a P. D. of 2.2 to 2.5 volts and current density 0.5 volts and current density 0.5 to 2 amps. per 100 sq. cms." On p. 67 we find, "Others forms of rotating electrodes. . . ." and again on p. 70, "the following method was worked by Ulsch," and lower down on the same page, "The anode is formed by a thin platinum wire which can be coiled round a glass rod to make rigid." On p. 94 we read, "It is important for this purpose, that the platinum electrodes should be well platinised in order to enable the solution of the gases." On p. 102 we find, "The value was relatively low with all the noble metals and with iron and nickel, but increased with the more electro-positive metals: cadmium, tin, lead, zinc and mercury, amounting in the lead case, to as much as 0.78 volt." On page 117 the following formula is given as that of azobenzene:



In a future edition the author will undoubtedly correct such mistakes as the above which seem to be almost inevitable in the first printing of a book. This manual of Dr. Pring's will be a welcome addition to the list of reference books which have already proven useful in laboratory instruction in physical chemistry.

FREDERICK H. GETMAN

VOL. XLVIII OCTOBER, 1912 NO. 4

AMERICAN

CHEMICAL JOURNAL

ON THE ACTION OF AQUEOUS SOLUTIONS OF ACIDS ON ALKENES

BY ARTHUR MICHAEL AND ROGER F. BRUNEL

[SECOND PAPER ON THE LAWS OF ADDITION IN ORGANIC CHEMISTRY[1]]

In examining the action of aqueous solutions of acids on alkenes we were led to question certain results obtained by Scheschukow[2] with regard to the action of aqueous hydriodic acid on isobutene. Scheschukow's statement was that if isobutene is passed through aqueous hydriodic acid saturated at 0° addition of the acid to the hydrocarbon with formation of tertiary butyl iodide takes place provided the acid has a greater concentration than that represented by $2HI + 11H_2O$ (1.7 specific gravity), but that at that concentration the reaction stops, i. e., isobutene ceases to take up hydriodic acid from the solution when the latter has the concentration of the stable hydrated acid.[3]

According to Roscoe[4] such a solution, at a pressure of 774 mm., contains 57 per cent. of hydriodic acid and distils unchanged at 127°; change of pressure alters the boiling point and consequently the composition of the distillate, but the effect is not great. Roscoe and Dittmar[1] showed that the liquid obtained by distillation at any temperature has the same composition as that obtained by passing air or hydrogen for some time through the solution at the same temperature. Roscoe thought the change in composition with pressure sufficient evidence against the existence of such solutions as definite compounds, but with compounds of such an unstable nature this conclusion does not necessarily follow. However, a consideration of the vapor pressure diagram[2] shows that the particular composition of the highest boiling solution, being that at which the mixture of vapors has the same composition as the residual solution, is merely a matter of chance. Such a solution of highest boiling point or minimum vapor pressure will exist in general when the vapor of each constituent is readily soluble in the other constituent. This great solubility is doubtless an indication of affinity between such constituents and of a tendency to form more or less definite compounds, but the composition of the highest boiling solution has no evident connection with that of any compound that may exist in the solution. Scheschukow's statements, if correct, would raise doubt as to the soundness of the above reasoning, since they seemed to give evidence of the existence of a compound of the composition $2HI.11H_2O$, but on repeating his experiments we find that his observations are not correct.

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[1] THIS JOURNAL, **41**, 118 (1909).

[2] Ber. d. chem. Ges., **19**, Ref. 544 (1886). Bull. soc. chim., [2] **42**, 329; **46**, 823. The original paper (J. Russ. Phys. Chem Soc., **1886**, I, 204) is not accessible to us.

[3] Bineau: Ann. chim. phys., [3] **7**, 266.

[4] Ann. Chem. (Liebig), **116**, 203 (1860).

If isobutene is passed through aqueous hydriodic acid saturated at 0°, absorption is at first quite rapid and a layer of tertiary butyl iodide is soon formed. After a time the rate of absorption decreases and, if the experiment is stopped when the iodide is very slowly formed, an acid of about the specific gravity 1.7 is obtained. The addition, however, by no means ceases at that point, as will be seen from the following experiments.

Isobutene was passed through hydriodic acid of specific gravity 1.9, cooled in ice, and when the gas appeared to pass through unabsorbed the experiment was stopped. The solution was slightly turbid and was allowed to stand until it became clear. The specific gravity of the acid layer was found to be 1.664. With hydriodic acid of specific gravity 1.90 at 17°, when the rapid absorption was over the gravity of the acid solutions in three experiments was found to be 1.642, 1.678, and 1.675.[1] The above solution of specific gravity 1.678, on further passage of isobutene, slowly gave a layer of iodide. In another experiment an acid of gravity 1.623 was used, and after 1.3 liters of isobutene were passed through it in two hours, the gravity had diminished to 1.588; a layer of iodide had formed and the acid solution contained some tertiary butylcarbinol. Similar results were obtained with freshly prepared solutions of hydriodic acid having the specific gravities 1.63 and 1.618. It is evident that although the velocity of solution decreases considerably when the concentration of about 60 per cent. hydriodic acid is reached, absorption does not cease; moreover, the rate of formation of a layer of the butyl iodide is no longer a criterion for the rate of absorption of the gas, as at that point part of the hydrocarbon dissolves, with formation of the soluble, tertiary carbinol.

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[1] Ann. Chem. (Liebig), **112**, 347 (1859).

[2] Nernst: Theoret. Chem. (6te Auflage), 110.

We then made similar experiments with trimethylethylene and hydrobromic acid. These were carried out in small sealed tubes, which were shaken, in some cases for only a few hours, but usually for some days or even weeks. When carbinol alone was formed the end of the reaction could be recognized by complete solution of the hydrocarbon; when bromide was formed the reaction could be followed by titration of the acid remaining. Only 1–3 cc. of acid were used in each experiment, the measurements being made with a 1 cc. burette graduated to 0.01 cc. When the amylene formed partly bromide and partly carbinol the amount of bromide was determined by titration of the residual acid and the rest was assumed to have formed carbinol, there being no other obvious possibility.

In the following table, Column 2 gives the ratio in molecules of water to hydrobromic acid in the solution used, and Column 6 the same ratio after the reaction. Column 5 shows what percentage of the hydrocarbon was converted into bromide. An excess of acid was used, as shown in Column 3, in order to avoid a decided change in concentration during the reaction. In experiments where two times are given[1] they refer to two experiments with the concentration concerned:

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[1] According to Roscoe the solution of minimum vapor pressure at 17° has a composition of 60.5 per cent., or a specific gravity a little over 1.71.

Table I

Normality of acid	H_2O : HBr Mols.	HBr : C_5H_{10} Mols.	Time Hours	Time Hours	Bromide Per cent.[2]	H_2O : HBr in resid. sol.
9.66	4.4	5.0	10	24	91–92	5.4
8.06	5.47	4.0	40	64	76	6.7
7.64	5.99	5.0	40	72	69	6.9
6.98	6.5	5.0	16	90	67	7.5
5.54	8.51	4.4	3	3	2	8.3
4.56	10.8	6.0	4		0	10.6

It will be noted that a 9.66 N acid forms largely bromide; one more dilute than 5.54 N only carbinol;[3] intermediate concentrations, mixtures of the two compounds. From the concentrations of the residual acids we may conclude that a solution of about $8H_2O : 1HBr$ would form carbinol and bromide in the ratio in which the water and acid are present.

With regard to the mechanism of the reaction there are three possibilities, disregarding the question of ionization. First, the carbinol may in all cases be formed first and then react with the acid to a greater or less extent, forming bromide; secondly, the acid may always add directly, so that the bromide is the intermediate product; and, lastly, both the water and acid may act simultaneously. We have no conclusive evidence for either view, but the following facts have some bearing on the question.

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[1] The times given in the table do not indicate the time required for the reaction to reach an end, but are given merely to show that times far enough apart were chosen to prove that the reaction had reached completion. Apparently, however, the rate of solution or reaction of the hydrocarbon decreases steadily from the most to the least concentrated solution.

[2] As will be seen from the experimental details below, the result given in the table is the means of results agreeing within the limits of accuracy of the method used.

[3] These are not the minimum and maximum concentrations, respectively, at which these results would be obtained, but are merely those of solutions made up arbitrarily beforehand which gave these results.

That the carbinol should always be the intermediate product seems very improbable when all the facts are considered. Tertiary amyl alcohol reacts with aqueous hydrobromic acid almost instantaneously, giving the corresponding bromide, provided the concentration of the acid is great enough so that it will react at all. If the amylene is converted into bromide by aqueous acids through the two steps amylene ⟶ carbinol ⟶ bromide, it must, therefore, be the first stage of the reaction that determines its velocity. The hydrocarbon, like the other alkenes, does not dissolve at all in pure water, so that the acid is evidently necessary as a catalytic agent. A very slight amount of acid is sufficient to cause the solution to take place slowly, and the rate increases, as would be expected, with the concentration of the catalyzing acid. The fact that is hard to explain, however, is that the velocity of solution—or reaction—continues up to the point where the concentration of acid is so great that there is very little water present. The reaction with pure, i. e., gaseous, hydrobromic acid is of course not comparable with that where the aqueous solutions are concerned; but if we use solutions of sulphuric acid we find that the rate of reaction increases with the concentration of the acid right up to acid of nearly 100 per cent. It would have to be a very marked catalytic effect on the part of the acid that would bring about a reaction of such great velocity when the concentration of the water becomes so small.

With regard to the second possibility, i. e., the intermediate formation of bromide, that also is possible as far as the reactivity of the bromide with water is concerned. Michael and Leupold[1] have shown that if tertiary amyl bromide is shaken with water it is dissolved in a half hour. In the solutions where the amylene dissolves, giving carbinol with greatest rapidity (4.56–5.54 N), the time required is several hours, which is thus long enough for the bromide, if formed, to be decomposed. It is to be noted, however, that all acids appear to catalyze the formation of tertiary alcohol from the amylene, whereas some of them are incapable of forming addition products with the hydrocarbon, such, for, example, as benzenesulphonic acid (see below). Here the reaction would appear to be directly with the water.

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[1] Ann. Chem. (Liebig), **379**, 290 (1911).

It seems probable, therefore, that the hydrocarbon reacts with both the water and acid simultaneously. But the familiar test for such side reactions, i. e., the examination of the ratio of the products at intervals as the reaction progresses to see if it is constant, cannot be applied here, since the products, the carbinol and the bromide, are convertible into each other with a velocity at least as great as that of their formation from the amylene, so that the examination of these products gives us data only for the esterification equilibrium between them and the acid and water.

As seen in Table I, with an acid of a strength somewhere between $HBr + 6.5H_2O$ and $HBr + 8.5H_2O$, there would be no change in the ratio of acid to water during the addition. The high heat of solution of hydrobromic acid in water indicates the formation of compounds,[1] and it may be that some such product with the composition of about $HBr : 8H_2O$ represents the most stable system that these substances are capable of forming, for it is very improbable that such products are altogether definite in composition. When a considerable excess of water or acid is present, it then reacts more readily than either of them, when they are in the proportion of the comparatively stable product or system. At that particular point the alkene should act with amounts of water and acid in the same ratio, which would be the case, as pointed out above, with an acid of about the composition $HBr : 8H_2O$. This concentration is quite different from that of a constant boiling acid, which is $HBr : 5H_2O$.

An explanation of these relations may perhaps be found in the assumption that the formation of halide or carbinol from amylene proceeds with union of the acid + water to a binary "polymolecule," which, with the hydrocarbon, forms a larger ternary "polymolecule."[2] Since there is an accumulation of free *chemical* energy in the formation of the ternary "polymolecule" it is able to do work that cannot be done by free amylene alone, which explains why acids, as well as water, act catalytically in these addition reactions. Further, since the solution of hydrobromic acid in water is exothermic, to effect the second stage of the reaction, that is, the breaking down of the ternary "polymolecule" into halide or carbinol and acid + water, a chemical hindrance has to be overcome which is the separation of a molecule of either acid or water from the binary part of the "polymolecule." If the acid is present in a much greater proportion than water, it should be easier to eliminate a molecule of it than one of water, and, reversely, if water is present in large excess, a molecule of that compound should be easier to remove than one of acid. From this point of view, the decomposition of x "polymolecules" of $C_5H_{10}.HBr.8H_2O$, proceeds with the formation of $x/2$ molecules of halide and of carbinol, and any system containing acid in a greater or less relation should lead to the formation of halide in a greater or less proportion.

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[1] See Pickering: Phil. Mag., [5] **36**, 111 (1893).

[2] Michael and Leupold (Ann. Chem. Liebig, **385**, 257) have shown that tertiary amyl alcohol unites with water and strong mineral acids to form "polymolecules," which at about 75° decompose with separation of amylene. On shaking this mixture at ordinary temperature the amylene dissolves with formation of tertiary carbinol. These relations accord with the view that the carbinol is formed by the direct union of the hydrocarbon with water, the acid acting catalytically.

The combination of water with alkenes resembles the hydrolysis of methyl acetate and of sugar, and it seemed of interest to ascertain whether the catalytic effects of acids stand in the same relation to each other in the first as they do in the latter reactions. For this purpose, the velocity of solution of trimethylethylene and isobutene in dilute solutions of acids was examined. Solutions of hydriodic acid (2.045 N), of hydrobromic acid (2.065 N) and of hydrochloric acid (2.058 N) were prepared, whose concentration of hydrogen ions were approximately the same. Two cc. of each solution were sealed in a small tube with 0.06 cc. of amylene and the tubes shaken at the same time until solution was effected. This took place in 140 minutes with hydriodic acid, in 200 with hydrobromic acid, and in 300 with hydrochloric acid. In a second series, the temperature was somewhat different and the times were longer, 280, 480 and 700 minutes, respectively, but these results stand approximately in the same relation to each other as those obtained in the preceding series. Solutions were then prepared, which, in accordance with known conductivity data, should have been isohydric. According to the titrations, they varied less than 1 per cent. from the calculated values. The results are as follows: with hydriodic acid (2.576 N) solution of the amylene took place in 18 days; with hydrochloric acid (2.525 N) in 23 days; and with trichloroacetic acid (2.052 N) it was still incomplete after 40 days. In another series of experiments the following results were obtained: with hydriodic acid (2.509 N) 12 days; benzenesulphonic acid (2.420 N) came next and effected solution very little before hydrobromic acid (2.550 N), which required 13 days; and with trichloroacetic acid (2.063 N), a considerable part of the hydrocarbon was undissolved in that time. Solutions of sulphuric, oxalic and phosphoric acids were next made, which contained acid and water in the proportion of one to eighty and whose molecular normalities were 0.687, 0.673 and 0.677. Two cc. of acid were placed in a tube, the weight taken, liquid isobutylene added, the tube closed and again weighed. The sulphuric acid tubes contained 0.139 and 0.138 gram of isobutylene and solution took place in 7 days. The oxalic acid tubes with 0.131 and 0.134 gram hydrocarbon took 33 and 34 days; the phosphoric acid tube contained 0.139 gram isobutylene and was broken after 35 days, but only about one-half had dissolved in that time.

It will be observed that there is a rough agreement with the relations found by the hydrolysis methods, and therefore also with the ionization constants of the acids. The order of reactivity with strong mineral acids stands, however, in a closer relationship to that found by sugar inversion than it does to that found by ester hydrolysis, or to that found by conductivity. Thus, according to the latter method, the relation of the constants of hydrochloric to hydrobromic acid is 100 : 100.1; with the methyl acetate method it is 100 : 98; while with the sugar inversion method it is 100 : 111. By the last method is obtained a decidedly higher value for hydrobromic than for hydrochloric acid, which relation also obtains in the addition of water to amylene. With benzenesulphonic acid the catalytic influence in causing water addition to amylene stands slightly higher than that of hydrochloric acid, which is also the case in sugar inversion (104 to 100), while in the ester hydrolysis the values are nearly the same (99 to 100), and the conductivity method shows a decidedly lower value (74.8 to 100).

It is remarkable that the order in which hydriodic, hydrobromic and hydrochloric acids, in dilute solution, exert a catalytic influence in inducing the addition of water to amylene is the same as that of the facility of addition of the acids themselves to unsaturated hydrocarbons, and also that of the reactivity of these acids in converting carbinols into halides.[1] This relation could be explained by assuming that the formation of carbinol from alkene is not direct, but passes through that of the iodide, bromide and chloride, since the ease of conversion of these different alkyl halides by water into carbinol proceeds in the same order.

As shown above, there is an objection to this assumption in the inability of benzenesulphonic acid to form addition products with the alkenes.

If, as seems probable, the elimination of water from the "polymolecules" may be effected more easily when hydriodic acid is present than when hydrobromic acid, and still less easily when hydrochloric acid is present, the above relations in the addition of water to the hydrocarbons would be explained.

EXPERIMENTAL PART

For the repetition of Scheschukow's experiments, hydriodic acid from Kahlbaum, of specific gravity 1.90, was used. The specific gravities were determined in a 3 cc. pycnometer of the Sprengel type with thermometer fused in, easily capable of accuracy to less than 0.1 per cent. About 5 cc. of acid were used for each experiment. This was placed in a test tube and the gas passed in through a tube drawn out to a fine point. As the tertiary iodide is decomposed by aqueous hydriodic acid when the concentration is below about 1.7 specific gravity, the layer of iodide formed was separated, when it no longer increased fast, as completely as possible by a pipette. In some cases it was separated several times as the reaction progressed.

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[1] These relations do not agree with the assumption that the reactions in question proceed through ionization. The ease of addition appears to be determined by the chemical hindrance, i. e., the energy required to separate the halogen from hydrogen.

Trimethylethylene with Aqueous Hydrobromic Acid Solutions

The hydrobromic acid solutions for the following experiments were standardized by titration from a 1 cc. burette graduated to 0.01 cc. against potassium hydroxide from a 50 cc. burette, with methyl orange as indicator. In all experiments given below the alkali, unless otherwise stated, was 0.591 N. One gram of amylene is equivalent to 24.14 cc. of this solution. The ratio of water to acid is expressed in numbers of molecules; the per cent. of acid by weight. The tubes were filled, sealed and shaken vigorously for the time indicated. After the first few experiments, in case there was a layer of bromide formed on top of the acid solution, the latter (lower layer) was removed by a pipette and titrated; the oil was then shaken out with a little water, which was removed and added to the titrated solution and alkali again added to an end point. This was repeated until the titration of the wash water was either zero or constant for successive washings. As the tertiary amyl bromide is slowly decomposed on shaking with water, the titration of this wash water was not zero if the shaking with the oil was prolonged. Only the final end points are given below, but it is indicated whether or not such a washing process was carried out. The difference between the alkali used for titration and that which would neutralize all the acid used is equivalent to the amyl bromide formed. The difference between this amount of alkali and that which would correspond to all the amylene taken is equivalent to the amylene converted into carbinol.

HBr 9.66 N. *$4.4H_2O$: 1HBr* (*50.8 Per cent. HBr*).—Two tubes were prepared each containing 0.210 gram amylene and 1.555 cc. acid (= 25.41 cc. KOH), i. e., 5 molecules of acid:

	I	II
Time	10 hrs. (oil not washed)	24 hrs. (oil not washed)
KOH to titrate	20.72	20.80
KOH = bromide formed	4.69	4.61
KOH = amylene taken	5.08	5.08
KOH = carbinol formed	0.39	0.47
Per cent. bromide	92.0	91.0

Residual acid (mean) $5.17H_2O$: 1HBr

HBr 8.06 N. $5.47H_2O : 1HBr$ (45.1 Per cent. HBr).—Two tubes were prepared, each containing 0.225 gram amylene and 1.600 cc. acid (= 21.82 cc. KOH), i. e., about 4 molecules of acid.

	I	II
Time	40 hrs. (oil not washed)	64 hrs. (oil washed)
KOH to titrate	17.60	17.73
KOH = bromide formed	4.22	4.09
KOH = amylene taken	5.43	5.43
KOH = carbinol formed	1.21	1.34
Per cent. bromide	77.7	75.3

Residual acid (mean) $6.7H_2O : 1HBr$

HBr 7.64 N. $5.99H_2O : 1HBr$ (42.9 Per cent. HBr).—Two tubes each with 0.200 gram amylene, 1.890 cc. acid (= 24.30 cc. KOH), i. e., 5 molecules of acid.

	I	II
Time	72 hrs. (oil washed)	40 hrs. (oil washed)
KOH to titrate	21.02	21.02
KOH = bromide formed	3.28	
KOH = amylene taken	4.82	Same as I
KOH = carbinol formed	1.54	
Per cent. bromide	68.1	

Residual acid, $6.9H_2O : 1HBr$

HBr 6.98 N. $6.5H_2O : 1HBr$ (40.8 Per cent. HBr).—Two tubes, each with 0.200 gram amylene, 2.000 cc. acid (= 23.62 cc. KOH), i. e., 4.9 molecules HBr.

	I	II
Time	16 hrs. (oil not washed)	90 hrs. (oil washed)
KOH to titrate	20.45	20.32
KOH = bromide formed	3.17	3.30
KOH = amylene taken	4.82	4.82
KOH = carbinol formed	1.65	1.52
Per cent. bromide	65.8	68.6

Residual acid (mean), $7.48H_2O : 1HBr$

HBr 5.54 N. $8.51H_2O : 1HBr$ (34.3 Per cent. HBr).—Two tubes were prepared, each with 0.200 gram amylene and 2.000 cc. acid (= 18.74 cc. KOH), i. e., 3.9 molecules HBr. A homogeneous solution was formed in less than 3 hours.

	I	II
Time	20 hrs.	3 hrs.
KOH to titrate	18.67	18.60
KOH = bromide formed	0.07	0.14
KOH = amylene taken	4.83	4.83
KOH = carbinol formed	4.76	4.69
Per cent. bromide	1.4	3.0

Residual acid (mean), 8.3H_2O : 1HBr

HBr 4.56 N. 10.8H_2O : 1HBr (29.5 Per cent. HBr).—One tube with 0.100 gram amylene, 1.886 cc. acid (= 99.43 cc. 0.0865 N KOH), i. e., 6 mols. HBr.

	I
Time	4 hrs.
KOH to titrate	99.62
KOH = bromide formed	0.00
KOH = amylene taken	16.57
Per cent. bromide	0.0

Residual acid, 10.6H_2O : 1HBr

In all cases above where much carbinol was formed, the solution, after titration, was distilled and the carbinol salted out from the first portion of the distillate by potash. In all experiments also the oil was distilled. The boiling point, where the amount was sufficient to give it with fair accuracy, was always from some point not below 95° or 100° to about 105°–108°. The boiling point of the tertiary alcohol is 101°–102°; that of the bromide 108°–109°.

Several experiments were carried out with tetramethylene and diisobutylene, but in all cases but one it was found that unchanged hydrocarbon was present, by the fact that complete solution in no case occurred.

HBr 8.06 N. 5.47H_2O : 1H_2O (45.1 Per cent. HBr).—Two tubes were prepared, each with 0.270 gram tetramethylethylene, 1.601 cc. acid (= 25.20 cc. KOH 0.5115 N), i. e., 4 molecules acid.

	I	II
Time	53 days (oil washed)	85 days
KOH to titrate	20.20	20.35
KOH = bromide formed	5.01	4.86
KOH = hexene used	6.28	6.28
KOH = carbinol formed	1.27	1.42
Per cent. bromide	80.0	77.4

Boiling Point of Oil.—About half distilled at near 120°, the rest went up to 130° or 135°. First lot redistilled and boiled at about 115°. Boiling point of the hexene, 72°; of tertiary hexylcarbinol, 117°; of bromide, about 135°–140°.

[Contributions from the Sheffield Laboratory of Yale University]

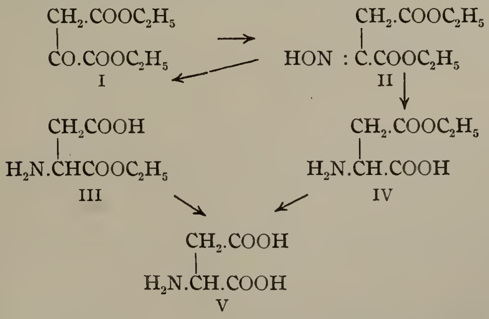
CCII —RESEARCHES ON PYRIMIDINES

THE ACTION OF HYDROXYLAMINE ON 4-METHYL-6-OXYPYRIMIDINE-2-OXALOTHIOGLYCOLLIC ACID. β-MERCAPTO-α-OXIMIDO-PROPIONIC ACID

By Treat B. Johnson and Norman A. Shepard

[FIFTY-SIXTH PAPER]

Piutti[1] synthesized aspartic acid from diethyl oxaloacetate in the following manner: The diethyl ester (I) was first converted into its oxime (II) and the latter then reduced, in an aqueous solution, with sodium amalgam. A mixture of the two isomeric esters, α-ethyl aspartate (III) and β-ethyl aspartate (IV), was obtained, which gave, by saponification, the inactive aspartic acid (V). This synthesis is represented by the following structural formulas:



The chief aim of the work described in this paper was to investigate the action of hydroxylamine on a mercapto derivative of diethyl oxaloacetate with the possibility of developing a synthesis of the unknown amino acid, *aminomercaptosuccinic acid* (VI).

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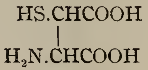
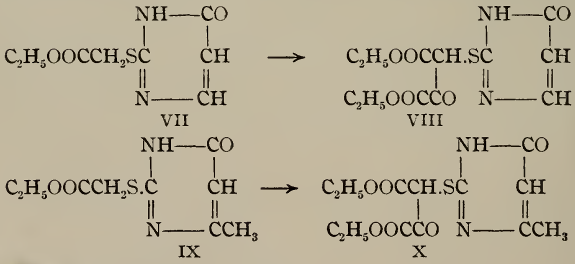
[1] Atti accad. Lincei, **1887,** 300. Gazz. chim. ital., **18,** 457. Ber. d. chem. Ges., **21,** Ref., 351. *Ibid.*, **22,** Ref., 241.



VI

$$\begin{array}{c} HS.CHCOOH \\ | \\ H_2N.CHCOOH \end{array}$$

In a previous paper from this laboratory[1] the writers have shown that diethyl oxalate condenses with certain pyrimidinethioglycollates, in alcohol solution and in the presence of sodium ethylate, forming the corresponding pyrimidineoxalothioglycollates. For example, ethyl 6-oxypyrimidine-2-thioglycollate (VII) and ethyl 4-methyl-6-oxypyrimidine-2-thioglycollate (IX) condensed with diethyl oxalate, forming diethyl 6-oxypyrimidine-2-oxalothioglycollate (VIII) and diethyl 4-methyl-6-oxypyrimidine-2-oxalothioglycollate (X), respectively. These β-ketone esters (VIII) and (X) represent new types of sulphur compounds, and, as we stated in our previous paper,[2] are of interest because of their possible use for further syntheses. The ester (X) is the foundation of this research and was selected for our work because it is a crystalline compound and can be prepared easily in large quantities.



VII VIII

IX X

Diethyl 4-methyl-6-oxypyrimidine-2-oxalothioglycollate (X) undergoes smoothly the acid and ketone hydrolyses typical of β-ketone esters. When warmed with alkali it undergoes saponification, oxalic acid is detached and 4-methyl-6-oxypyrimidine-2-thioglycollic acid (XII) is formed. On the other hand, when digested with hydrochloric acid, ethyl chloride is evolved and the dibasic acid (XI) is produced. This acid, however, is unstable and loses carbon dioxide on long digestion and is transformed quantitatively into the pyruvic acid derivative, 4-methyl-6-oxypyrimidine-2-thiopyruvic acid (XIII). It is a remarkable fact that this acid (XIII) is so stable in the presence of boiling hydrochloric acid while the corresponding 2-thioglycollic acid (XII) is transformed quantitatively, under the same conditions, into thioglycollic acid and methyluracil (XIV):

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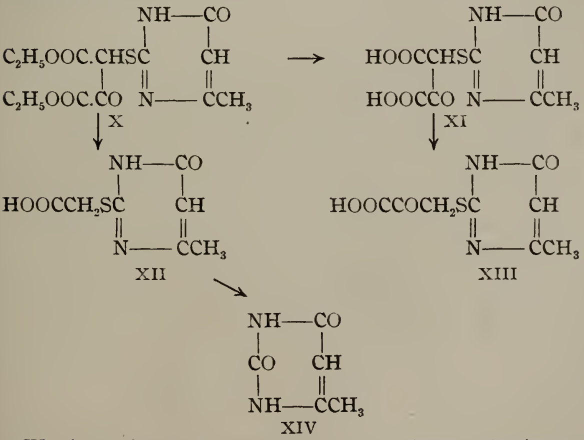
[1] This Journal, **46**, 346.

[2] *Loc. cit.*



We have investigated the action of hydroxylamine on 4-methyl-6-oxypyrimidine-2-oxalothioglycollic acid (XI), its diethyl ester (X) and also 4-methyl-6-oxypyrimidine-2-thiopyruvic acid (XIII). We find that the dibasic acid (XI) reacts with hydroxylamine, giving three definite compounds. The primary product of the reaction is apparently the oxime (XVIII) corresponding to oximidosuccinic acid (XV), which has been described by Hantzsch and Cramer.[1] This oxime, however, was not isolated. It was unstable and lost a molecule of carbon dioxide, at ordinary temperature, forming the oxime of 4-methyl-6-oxypyrimidine-2-thiopyruvic acid (XX). This manner of decomposition is unique, since the prototype of this series of acids, oximidosuccinic acid (XV), which occurs in two stereoisomeric modifications, breaks down in an entirely different way with formation of water, carbon dioxide and cyanoacetic acid (XVII).[1] We obtained no evidence of the formation of any 4-methyl-6-oxypyrimidine-2-cyanoacetic acid (XIX) or the oximido acid (XXI). In other words, it is the carboxyl group in the β-position with respect to the oxime group which is detached in the pyrimidine derivative (XVIII), while it is the α-carboxyl which is detached in the case of Cramer's oximidosuccinic acid (XV). Cramer[2] writes as follows: "Dieser Zerfall der β-Oximidobernsteinsäure vollzieht sich aber merkwürdigerweise bereits bei gewöhnlicher Temperatur und bei der vollständig trockenen Substanz. Die frisch bereitete Säure nimmt beim Stehen im Exsiccator über Kali anfangs rasch, schliesslich langsam an Gewicht, ab; doch konnte die Zersetzung nicht bis zu Ende verfolgt werden, da die Substanz mit Eisenchlorid sich immer noch blau färbte, also noch unveränderte β-Oximidobernsteinsäure enthielt."

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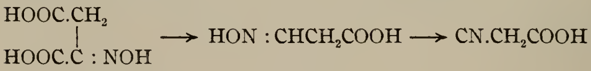
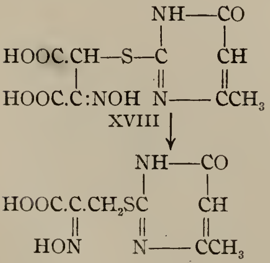
[1] Ber. d. chem. Ges., **24**, 1192, 1198.



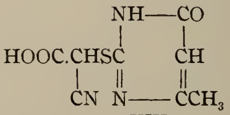
$$\begin{array}{l} HOOC.CH_2 \\ \quad | \\ HOOC.C:NOH \end{array} \longrightarrow HON:CHCH_2COOH \longrightarrow CN.CH_2COOH$$

XV XVI XVII

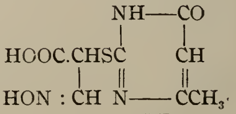


XVIII

XX



XIX



XXI

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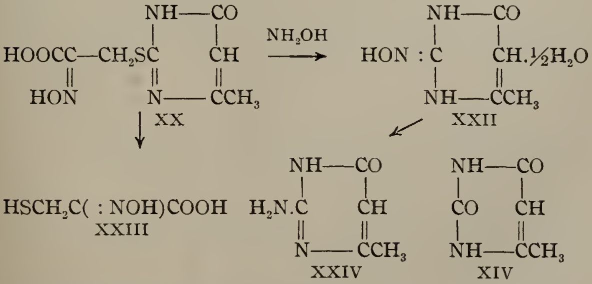
[1] Hantzsch and Cramer: *Loc. cit.*

[2] Ber. d. chem. Ges., **24**, 1207.

This difference in the behavior of these two acids is truly remarkable. These interesting changes are represented by the above formulas.

That we were dealing with the α-oximido acid (XX) and not with a β-derivative (XXI) corresponding to the β-oximidopropionic acid (XVI)[1] was established by the following facts: We stated above that the oxalothioglycollic acid (XI) reacts with hydroxylamine to form not only the oxime (XX) but also two other derivatives. We find that the pyruvic acid (XIII) reacts with hydroxylamine and forms the same substances as are obtained from the oxalothioglycollic acid (XI). While the oxime (XX) could be isolated and purified, on the other hand it is unstable in the presence of free hydroxylamine. Under these conditions, the bond between the sulphur and carbon in the pyrimidine nucleus is ruptured and β-mercapto-α-oximidopropionic acid (XXIII) and 2-oximido-4-methyl-6-oxypyrimidine (XXII) are formed quantitatively. These derivatives are of interest as they are representatives of two new types of organic compounds. The formation of the same substances from the pyruvic acid (XIII) and the oxalothioglycollic acid (XI) is proof, therefore, that the oxime (XVIII) loses that carboxyl group which is joined to the —CHS— grouping. An attempt to reduce the oximidopyrimidine (XXII) to 2-amino-4-methyl-6-oxypyrimidine (XXIV) with stannous chloride in hydrochloric acid solution was unsuccessful. The oxime underwent hydrolysis and methyluracil (XIV) was formed.



XX → XXII (with NH_2OH) → XXIV, XIV; XX → XXIII

$HSCH_2C(:NOH)COOH$ XXIII

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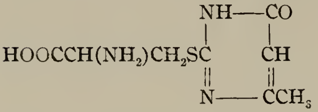
[1] Pechmann: Ann. Chem. (Liebig), **264**, 286. Hantzsch: Ber. d. chem. Ges. **25**, 1904.

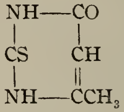
We have now investigated the behavior, towards reducing agents, of the two oximes, β-mercapto-α-oximidopropionic acid (XXIII) and its pyrimidine derivative (XX). We have reduced these two acids in alkaline, acid and neutral solutions, but in no case did we succeed in obtaining cysteine (XXV), or the pyrimidine derivative of this amino acid (XXVI). On the other hand, both acids are unstable and undergo complete decomposition with reduction of the β-mercapto groupings and the α-oximido groups with formation of alanine. The sulphur was obtained in the form of hydrogen sulphide and 2-thio-4-methyluracil (XXVII), respectively. While we obtained conclusive evidence of the formation of alanine, the yield of this acid, however, was extremely small. This is explained by the fact that the greater portion of the oximido acids undergoes hydrolysis, before reduction, with formation of hydroxylamine, which is then reduced to ammonia. The reduction of the oximido acid (XX) is expressed by the following equation:

$HS.CH_2.CH.(NH_2).COOH$

XXV



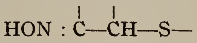
XXVI



XXVII

$$HOOCC(: NOH)CH_2S.(C_5H_5ON_2) + 3H_2 = CH_3CH(NH_2)COOH + H_2O + C_5H_5ON_2S$$

The investigation of oximes containing the grouping

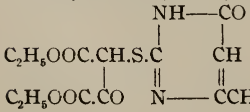


$$HON : \overset{|}{C}—\overset{|}{C}H—S—$$

will be continued.

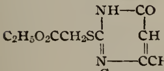
EXPERIMENTAL PART

Diethyl 4-Methyl-6-oxypyrimidine-2-oxalothioglycollate,



.—This pyrimidine has been described in a previous paper from this laboratory.[1] Since it was the starting point for our investigation we have had occasion to prepare it several times and consequently will give here the best conditions for preparing it in large quantities. One molecular proportion of ethyl 4-methyl-6-oxypyrimidine-2-thioglycollate[1] is dissolved in 5 parts of absolute alcohol containing 2.25–2.5 atoms of sodium in the form of sodium ethylate. One and one-half molecular proportions of diethyl oxalate are then added to the cool solution and the mixture allowed to stand, protected from the air, at ordinary temperature. Working with 10 grams of thioglycollate at a time, it has been our experience that the condensation is complete in about 20 hours. In most cases, however, we allowed the reaction to proceed for a much longer time. In one experiment, for example, from 30.0 grams of the glycollate we obtained 34.0 grams of the pure condensation product, corresponding to 80.0 per cent. of the theoretical yield. After the condensation was complete an excess of ether was then added to the mixture, when the yellow sodium salt of the ketone ester deposited in a granular condition. This salt is very hygroscopic and dissolves immediately in cold water. The pyrimidine was obtained by addition of acetic acid, in slight excess, to this aqueous solution of its sodium salt. It deposited in colorless prisms, which melted without further purification at 138°–139°. A mixture of this substance with the original thioglycollate melted at 125°–130°. It was purified by recrystallization from alcohol and melted at 140°. It separated from alcohol in characteristic, hexagonal tables or prisms. The results of six of our experiments are recorded in the following table:

Table I

	 Grams	$COOC_2H_5$ $COOC_2H_5$ Grams	Sodium Grams	Time	Yield of pyrimidine Grams	Per cent. of theory
1	20.0	19.2	4.0	6 days	22.5	78.4
2	40.0	38.4	8.0	12 days	36.0	62.7
3	40.0	38.4	8.0	15 days	40.0	70.0
4	10.0	9.6	2.5	20 hours	10.7	74.8
5	10.0	9.6	2.5	20 hours	10.7	74.8
6	30.0	28.8	6.75	5–6 days	34.0	80.0

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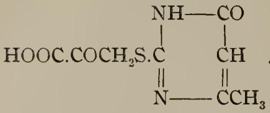
[1] Johnson and Shepard: *Loc. cit.*

4-Methyl-6-oxypyrimidine-2-thiopyruvic Acid,

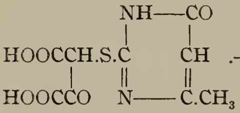


$$\begin{array}{lll} & \mathrm{NH} & \text{—}\mathrm{CO} \\ & | & | \\ \mathrm{HOOC.COCH_2S.C} & & \mathrm{CH} \\ & \| & \| \\ & \mathrm{N} & \text{—}\mathrm{CCH_3} \end{array}$$

.—This acid is easily prepared by hydrolysis of diethyl 4-methyl-6-oxypyrimidine-2-oxalothioglycollate with hydrochloric acid. Ten grams of the ester were dissolved in 20–30 cc. of concentrated hydrochloric acid and the solution evaporated to dryness on the steam bath. This operation was repeated twice, in each case with 20 cc. of hydrochloric acid. This pyruvic acid was thus obtained in a crystalline condition and melted without further purification at 180°–185°. It is soluble in hot water and difficultly soluble in boiling alcohol. It was purified, for analysis, by recrystallization from water and separated, on cooling, in hexagonal prisms, which melted at 210°–212° with effervescence. The yield was good. Analysis (Kjeldahl):

	Calculated for $C_8H_8O_4N_2S$	Found I	Found II
N	12.28	12.16	12.34

4-Methyl-6-oxypyrimidine-2-oxalothioglycollic Acid,



$$\begin{array}{lll} & \mathrm{NH} & \text{—}\mathrm{CO} \\ & | & | \\ \mathrm{HOOCCH.S.C} & & \mathrm{CH} \\ | & \| & \| \\ \mathrm{HOOCCO} \quad \mathrm{N} & & \text{—}\mathrm{C.CH_3} \end{array}$$

.—This dibasic acid can be obtained easily by careful hydrolysis of diethyl 4-methyl-6-oxypyrimidine-2-oxalothioglycollate. Twenty-two and four-tenths grams of this ester were suspended in 80 cc. of concentrated hydrochloric acid in an evaporating dish. On warming, it completely dissolved and ethyl chloride was evolved. The solution was then evaporated almost to dryness when the acid was obtained as a syrup, which immediately solidified on cooling. The crude acid melted at 150°–160°. It is extremely soluble in cold water and boiling alcohol, and insoluble in chloroform. It crystallizes from alcohol in rosettes of slender prisms, which melt at 159°–161° with evolution of carbon dioxide. The yield of purified material was generally from 70–80 per cent. of the theoretical. Analysis (Kjeldahl):

see errata p. 575

	Calculated for [redacted]	Found I	Found II
N	10.29	10.28	10.20

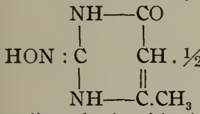
Action of Potassium Hydroxide on Diethyl 4-Methyl-6-oxypyrimidine-2-oxalothioglycollate

Four-tenths of a gram of potassium hydroxide was dissolved in 15–20 cc. of water and 2.0 grams of this pyrimidine dissolved in the solution. The mixture was then heated on the steam bath for one hour and finally cooled. Ethyl 4-methyl-6-oxypyrimidine-2-thioglycollate separated and melted at 145°-146°.

The Action of Hydroxylamine on 4-Methyl-6-oxypyrimidine-2-oxalothioglycollic Acid

Experiment 1

2-Oximido-4-methyl-6-oxypyrimidine,



$. \frac{1}{2}H_2O$.—Two and two-tenths grams of sodium hydroxide (3 mols.) were dissolved in 5 cc. of water and 5 grams of the oxalothioglycollate acid dissolved in the cold solution. A strong aqueous solution of hydroxylamine hydrochloride (1.5 mols.) was then added and the mixture allowed to stand at ordinary temperature. Hydrogen sulphide was evolved in small amount and finally this pyrimidine deposited in the form of colorless prisms arranged in burrs. The yield of crude material was 2.5 grams, or 96.1 per cent. of the theoretical. This pyrimidine is insoluble in absolute alcohol and cold water. It possesses the characteristic property of crystallizing from hot water in two crystalline modifications. On slow cooling and in not too concentrated solution it deposits in beautiful, stout blocks, while in very concentrated solutions and when cooled quickly it separates as prisms arranged in sheaves. Both forms were free from sulphur and melted at 225°–228° with violent effervescence. This melting point, however, varies according to the mode of heating. The pyrimidine gives no precipitate with picric acid or platinum chloride solution. It contains water of crystallization which was determined by heating at 130°–140°.

I. 0.4751 gram substance lost 0.0301 gram H_2O.
Nitrogen determinations (Kjeldahl):

	Calculated for $C_5H_7O_2N_3.\frac{1}{2}H_2O$	Found
H_2O	6.0	6.3
N	28.0	28.2, 28.3, 28.37, 28.1, 28.05, 28.38

Experiment 2

α-Oximido-β-mercaptopropionic Acid (*Oxime of Mercaptopyruvic Acid*, $HS.CH_2.C(:NOH)COOH$.—In this experiment we used 5 grams of 4-methyl-6-oxypyrimidine-2-oxalothioglycollic acid, 3 molecular proportions of hydroxylamine hydrochloride (4 grams) and 5 molecular proportions of sodium hydroxide (3.8 grams). The procedure was then exactly the same as in our first experiment. In this experiment, however, within one-half hour we obtained a magma of colorless needles. No attempt was made to identify this substance, but the mixture was allowed to stand at ordinary temperature. Within a few hours this crystalline material began to disappear, carbon dioxide was slowly evolved and finally balls of minute prisms began to form and deposit on the bottom of the flask. In about 5 days the transformation was complete and only the balls remained suspended in the liquid. This crystalline substance was identified as 2-oximido-4-methyl-6-oxypyrimidine described in the previous experiment. It exhibited the same characteristic behavior when recrystallized from hot water and decomposed with effervescence at 225°–228°. Analysis (Kjeldahl):

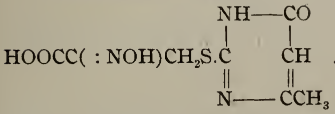
	Calculated for $C_5H_7O_2N_3.\frac{1}{2}H_2O$	Found
N	28.0	28.1

The aqueous filtrate (above) was carefully acidified with hydrochloric acid, when the oximidomercaptopropionic acid deposited in corpuscular crystals. The material contained sulphur and melted without further purification at 172°–173° with effervescence. The acid crystallizes from hot water in needlelike prisms, which decompose at 178°–180° with charring and effervescence. Analysis (Kjeldahl):

	Calculated for $C_3H_5O_3NS$	Found
N	10.37	10.13

Experiment 3

4-Methyl-6-oxypyrimidine-2-oximidothiopropionic Acid,



.—In this experiment we used 15 grams of 4-methyl-6-oxypyrimidine-2-oxalothioglycollic acid and subjected it to exactly the same treatment as in Experiment 2. There was an immediate reaction and within 30 minutes a magma of colorless needles was obtained. These were separated by filtration and dried in a desiccator over sulphuric acid (filtrate saved). This substance was a sodium salt and decomposed at 195°–200° with effervescence. It was not analyzed. The salt was very soluble in cold water and on adding hydrochloric acid to the aqueous solution the oximido acid deposited at once. This acid was purified by crystallization from boiling absolute alcohol and separated, on cooling, in clusters of prisms which melted at 160°–161° with effervescence. This melting point, however, varies according to the mode of heating. If heated slowly in a sulphuric acid bath the acid will decompose at about 150°. This compound exhibits pyro-electric properties. The yield of crude acid was 6.5 grams. Analyses (Kjeldahl):

	Calculated for $C_8H_9O_4N_3S$	Found I	Found II
N	17.28	17.10	17.22

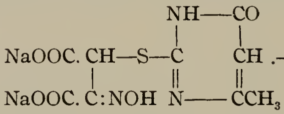
The aqueous filtrate (above) was allowed to stand at ordinary temperature, when a small amount of 2-oximido-4-methyl-

6-oxypyrimidine separated. It melted after one crystallization from water at 225°–228°. Analysis (Kjeldahl):

	Calculated for $C_5H_7O_2N_3 . \frac{1}{2}H_2O$	Found
N	28.0	28.3

After separating the above oxime the aqueous filtrate was then acidified with dilute hydrochloric acid, when there was a slight evolution of hydrogen sulphide and α-oximido-β-mercaptopropionic acid separated. The crude acid melted at 174°–175°. The yield was small.

Experiment 4

Sodium Salt of 4-Methyl-6-oxypyrimidine-2-oximidothiosuccinic Acid,  .—In this experiment we used the following proportions: 5 grams of the oxalothioglycollic acid, 3 grams of sodium hydroxide (4 mols.) and 1.3 grams of hydroxylamine hydrochloride (1 mol.). Otherwise the procedure was the same as in the preceding experiments. After standing for about 30 hours, the solution was then acidified (cold) with dilute hydrochloric acid. This sodium salt deposited at once as a colorless powder. It was separated, washed and then dried in a desiccator. It was soluble in water and insoluble in alcohol. It decomposed at about 200° with effervescence. Nitrogen determination (Kjeldahl):

	Calculated for $C_9H_7O_6N_3SNa_2$	Found
N	12.6	12.42

An attempt to prepare the pure oximido acid from this salt was unsuccessful. The salt was dissolved in water and the solution acidified strongly with hydrochloric acid, when a colorless crystalline substance separated, which decomposed with violent effervescence at 153°–155°. The yield was 2 grams and a nitrogen determination on the crude material indicated a mixture of the oxime of the dibasic acid and 4-methyl-

6-oxypyrimidine-2-oximidothiopropionic acid. We found 15.7 per cent. of nitrogen while the calculated value for the dibasic acid is 17.28 per cent., and that for the monobasic acid is 14.6 per cent. After crystallization from alcohol the pure oxime of the monobasic acid (previously described) separated in clusters of prisms and decomposed at 158° with effervescence. Analysis (Kjeldahl):

	Calculated for $C_8H_9O_4N_3S$	Found
N	17.28	17.4

In a fifth experiment in which 3 molecular proportions of hydroxylamine hydrochloride and 5 proportions of sodium hydroxide were used we obtained not only the α-oximido-β-mercaptopropionic acid in good yield, but also succeeded in isolating as by-products small amounts of 2-thio-4-methyluracil and 4-methyluracil.

The Action of Hydroxylamine on 4-Methyl-6-oxypyrimidine-2-thiopyruvic Acid

Two and one-half grams of pyruvic acid and 2 grams of potassium hydroxide (3 mols.) were dissolved in cold water and 2 molecular proportions of hydroxylamine hydrochloride added to the solution. The mixture was then allowed to stand for about 4.5 hours, when the reaction was apparently complete. 2-Oximido-4-methyl-6-oxypyrimidine had separated and was purified by crystallization from hot water. It melted at 225°–228° with violent effervescence and the yield was practically quantitative.

The filtrate above, which was neutral to turmeric and litmus, was acidified with hydrochloric acid, when we obtained an immediate precipitate. The substance was identified as α-oximido-β-mercaptopropionic acid and melted at 178°–180° with effervescence. A mixture of this substance and some of the oximido acid prepared in Experiment 2 above melted at the same temperature. It contained sulphur, but was free from chlorine. Analysis (Kjeldahl):

	Calculated for $C_3H_5O_3NS$	Found
N	10.3	9.97

The Behavior of 4-Methyl-6-oxypyrimidine-2-oximidothiopropionic Acid, $HOOCC(:NOH)CH_2S(C_5H_5ON_2)$, on Reduction

I. Reduction with Stannous Chloride and Hydrochloric Acid.—Six grams of stannous chloride were dissolved in a mixture of 40 cc. of water and 20 cc. of dilute hydrochloric acid. Three grams of the oxime were then added and the acid heated to 55°–60°. The oxime dissolved, forming a light yellow solution, and hydrogen sulphide was slowly evolved. After heating for one hour at 50° the mixture was diluted with water and the tin precipitated as sulphide with hydrogen sulphide. After removal of the tin the filtrate was then evaporated to dryness by heating at 45°–50° under diminished pressure. We obtained a crystalline residue, which contained both chlorine and sulphur. The substance was insoluble in alcohol but dissolved in hot water and, on cooling, clusters of needles deposited, which decomposed when heated above 275°. This product contained no chlorine or sulphur and was identified as 4-methyluracil. The filtrate from the 4-methyluracil gave a strong test for chlorine, and, when made alkaline with dilute sodium hydroxide solution and warmed, ammonia was evolved. This result proved the presence of ammonium chloride, indicating that the oxime was hydrolyzed during the reduction and the hydroxylamine then reduced to ammonia. No other decomposition product was identified.

II. Reduction with Zinc Dust and Formic Acid.—Three grams of the oxime and an excess of zinc dust were suspended in 100 cc. of formic acid of specific gravity 1.2. The oxime slowly dissolved and hydrogen sulphide was evolved immediately. The reduction was continued for 5 days at ordinary temperature, when the mixture was diluted copiously with water and the excess of zinc precipitated with hydrogen sulphide. After filtering from undissolved zinc and the zinc sulphide, the solution was then evaporated to dryness, the residue dissolved in water and the last traces of zinc precipitated as sulphide. On evaporating the solution to dryness again we obtained a crystalline residue, which was purified by crystallization from boiling water. On cooling, flat prisms separated, which did not melt or decompose below 280°. This substance contained sulphur and was identified as 2-thio-4-methyluracil. Analysis for sulphur (Carius):

I. 0 0908 gram substance gave 0.1520 gram $BaSO_4$.

	Calculated for $C_5H_6ON_2S$	Found
S	22.53	22.9

After the separation and purification of the methylthiouracil the filtrates were combined, concentrated and then subjected to the Baumann and Schotten reaction with 5 grams of benzoyl chloride and an excess of sodium bicarbonate. After the benzoyl chloride had disappeared the solution was acidified with hydrochloric acid, when a crystalline precipitate was obtained. This was separated, dried and then digested with ligroin to remove benzoic acid. We obtained a small amount of insoluble material, which was purified by crystallization from hot water. It separated, on cooling, in prisms, which were badly etched and melted at 163°–165°. This melting point indicated that we were dealing with benzoylalanine. Fischer[1] states that this acid melts at 165°–166°. We did not obtain enough of the pure acid for analysis.

III. Reduction with Aluminium Amalgam.—In this experiment the oxime was dissolved in about 90 per cent. alcohol and an excess of aluminium amalgam suspended in the solution. The reduction was continued for two days. Hydrogen sulphide was slowly generated. After filtering from aluminium hydroxide the filtrate was evaporated to dryness, when a crystalline residue was obtained. This was first triturated with cold, dilute hydrochloric acid to remove any base present and the insoluble material purified by crystallization from hot water. The product that separated here appeared to be a mixture of 4-methyluracil and 4-methyl-2-thiouracil. By repeated recrystallizations from water the thiouracil was finally separated sufficiently pure for analysis. It did not melt below 300° and a nitrogen determination (Kjeldahl) gave:

	Calculated for $C_5H_6ON_2S$	Found
N	19.7	19.36

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[1] Ber. d. chem. Ges., **32**, 2454.

When the hydrochloric acid solution above was evaporated a syrupy residue was obtained. This was shaken with benzoyl chloride and alkali but we did not succeed in isolating any benzoylalanine.

Reduction of 2-Oximido-4-methyl-6-oxypyrimidine

One gram of the oxime and 2 grams of crystalline stannous chloride were dissolved in dilute hydrochloric acid and the solution heated on the steam bath for 30 minutes. The solution was then evaporated to dryness to remove hydrochloric acid, the residue dissolved in water and the tin precipitated with hydrogen sulphide. After filtering off the tin sulphide the solution was concentrated and cooled, when 4-methyluracil separated. We obtained no evidence of the formation of 2-amino-4-methyl-6-oxypyrimidine, the oximido group having been detached as hydroxylamine. Analysis (Kjeldahl):

	Calculated for $C_5H_6O_2N_2$	Found
N	22.2	21.95

The Action of Hydroxylamine on Diethyl 4-Methyl-6-oxypyrimidine-2-oxalothioglycollate

Three molecular proportions of potassium hydroxide (5 grams) were dissolved in water and 10 grams of this pyrimidine dissolved in the cold alkali solution. Two molecular proportions of hydroxylamine hydrochloride were then added and the solution allowed to stand for 1.5 hours at ordinary temperature. A yellow solid had then deposited and was separated by filtration and the filtrate allowed to stand. The weight of this crystalline substance was 1.5 grams and it was identified as ethyl 4-methyl-6-oxypyrimidine-2-thioglycollate. It crystallized from alcohol in prisms and melted at 146° to a clear oil. The original solution, after standing about 12 hours longer, deposited 3.5 grams more of a crystalline substance. This was purified by crystallization from hot water and was identified as 2-oximido-4-methyl-6-oxypyrimidine. It melted at 224°–227° and a mixture of the compound with some of the pure oxime melted at the same temperature.

The Behavior of the α-Oximido-β-mercaptopropionic Acid, $HSCH_2.C(:NOH)COOH$, on Reduction

This compound undergoes complete decomposition in the presence of reducing agents and we obtained no evidence of the formation of cysteine or cystine. We used tin chloride, aluminium amalgam and zinc and formic acid, but in every case hydrogen sulphide was evolved immediately at ordinary temperature. We also did not observe a smooth formation of alanine. Not only is hydrogen sulphide evolved in the presence of reducing agents but the oxime undergoes hydrolysis with formation of hydroxylamine, which is then reduced to ammonia. The following experiment was performed with zinc and formic acid as the reducing agent: Five grams of the oximido acid and an excess of zinc dust were suspended in a mixture of 150 cc. of formic acid of specific gravity 1.2 and 50 cc. of specific gravity 1.12. Hydrogen sulphide was evolved immediately at ordinary temperature. After standing about 24 hours at ordinary temperature the mixture was then warmed on the steam bath for 5 hours and finally transferred to an evaporating dish and diluted copiously with alcohol. The alcohol and formic acid were then evaporated, the residue left behind triturated with warm water and an insoluble residue filtered off. This was identified as zinc sulphide. The filtrate was saturated with hydrogen sulphide to remove the zinc as sulphide, filtered and again evaporated to dryness after acidifying with hydrochloric acid. We obtained a crystalline deposit which contained a large amount of ammonium chloride. The ammonia was expelled by digestion with barium hydroxide solution, the barium precipitated by addition of the required amount of sulphuric acid and the solution then evaporated to dryness. We thus obtained about 1.5 grams of a partially crystalline residue, which was colorless and very soluble in water. This was dried at 100° and then warmed at 100°, in about 6 cc. of acetic anhydride, with 2.7 grams of potassium thiocyanate. There was an immediate reaction on warming, the solution assumed a red color and free thiocyanic acid was evolved. After heating for about 15 minutes and then pouring into cold water a viscous oil separated which finally solidified on standing. This was a very impure substance but finally a small amount of crystalline material was separated by crystallization from alcohol. It melted at 165°–168°, and gave a strong test for sulphur. We did not obtain enough of this substance for analysis but it was probably 2-thio-3-acetyl-4-methylhydantoin.[1]

New Haven, Conn.
July 2, 1912

[Contributions from the Sheffield Laboratory of Yale University]

CCIII.—RESEARCHES ON PYRIMIDINES

THE ACTION OF POTASSIUM THIOCYANATE ON PRIMARY HALIDES[2]

By Treat B. Johnson and Arthur J. Hill

[FIFTY-SEVENTH PAPER]

In the acyclic series an unsaturated condition in the 2,3-position of a halide $\underset{3}{\mathrm{C}} : \underset{2}{\mathrm{C}}.\underset{1}{\mathrm{CH}}.$ hal.— is favorable to the formation of an isothiocyanate, —NCS. For example, allyl iodide reacts with potassium thiocyanate to form the corresponding isothiocyanate or allyl mustard oil (I). Only a small number of such halides have been investigated, but, so far as examined, it is not possible to isolate the primary products of the reaction, *thiocyanates*, unless heat is avoided. We have also observed this same characteristic behavior when this unsaturated grouping functionates in the halides of the cyclic series. The pyrimidine imidechlorides corresponding to the formula $\underbrace{\mathrm{N.C.N.C : C.CCl}}$ contain this grouping and in every case which we have examined in this laboratory[3] the final product of the reaction with potassium thiocyanate was an isothio-

$$\mathrm{CH_2 : CH.CH_2I + KSCN = CH_2 : CH.CH_2SCN} \longrightarrow \underset{\mathrm{I}}{\mathrm{CH_2 : CH.CH_2NCS}}$$

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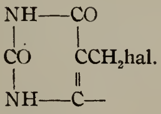
[1] Johnson: J. Biol. Chem., **11**, 97.

[2] By the term primary halide is meant a halide containing the grouping —$\mathrm{CH_2}$. hal.—T. B. J.

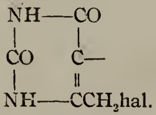
[3] This Journal, **33**, 448; **36**, 136; **40**, 132.

cyanate. We found, however, in some cases that the primary thiocyanates possessed remarkable stability and could be isolated and easily purified without rearrangement at ordinary temperature. In fact, these cases of molecular rearrangement, in the pyrimidine series, were unique for this type of change.

Two interesting types of pyrimidine halides, which have not been studied, are the halide derivatives of 4- and 5-methyldiketotetrahydropyrimidines, which may be represented by the formulas (II) and (III). The chemical evidence, so far obtained, indicates that these ketopyrimidines contain their double bond between the 4- and 5-positions of the ring. Therefore, their corresponding primary halides, (II) and (III), theoretically should react with potassium thiocyanate to form isothiocyanates. The primary object of the work described in this paper was to test this assumption. We shall give a description of the synthesis and behavior towards potassium thiocyanate of a primary halide corresponding to Type (III).



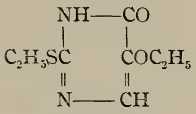
II



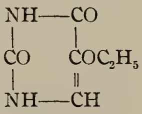
III

During the progress of an investigation by Mr. Hill on the mechanism of Claisen's condensation, we had occasion to investigate the action of metallic sodium on ethyl phenoxyacetate, $C_6H_5OCH_2COOC_2H_5$. We observed that the ester undergoes a normal condensation with formation of the sodium salt of ethyl α,γ-diphenoxyacetoacetate (IX). Ethyl β-naphthoxyacetate behaves in a similar manner, forming the sodium salt (XVIII). The yields of these two salts, however, were small, owing, apparently, to secondary reactions. We have now found unexpectedly that these condensations are influenced by the presence of certain reagents, which act catalytically. The yields of the salts (IX) and (XVIII) are thereby greatly increased and consequently we have been able to obtain them in sufficient quantity for experimental purposes.[1]

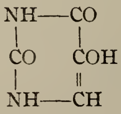
We have investigated the action of both of these salts on thiourea and find that they condense smoothly with formation of the corresponding pyrimidines, viz., 2-thio-4-phenoxymethyl-5-phenoxy-6-oxypyrimidine (XI) and 2-thio-4-naphthoxymethyl-5-naphthoxy-6-oxypyrimidine (XVI), respectively. Both pyrimidines are desulphurized quantitatively by digestion with chloroacetic acid, in aqueous solution, forming the corresponding diphenoxy- and dinaphthoxypyrimidines, (XII) and (XVII), respectively. Attempts to desulphurize these thiopyrimidines by alkylation and then hydrolysis of their corresponding mercapto derivatives, (X) and (XIII), were unsuccessful. The mercaptopyrimidines could be boiled with hydrochloric and hydrobromic acids for hours without decomposition. This behavior is in accord with previous observations. Johnson and McCollum,[2] for example, observed that the ethyl ether of isobarbituric acid (V) cannot be obtained by boiling 2-ethylmercapto-5-ethoxy-6-oxypyrimidine (IV) with hydrochloric or hydrobromic acid. By heating with hydrochloric acid in a bomb tube at 150° a mixture of the ethoxypyrimidine and isobarbituric acid (VI) was obtained.



IV



V



VI

In a recent paper, Johnson and Guest[3] have given a description of 5-phenoxyuracil and have shown that the phenoxy group is so firmly bound that this pyrimidine can be heated with hydrochloric acid at 160° without change. It was therefore of special interest to investigate the action of hydrochloric acid on the diphenoxypyrimidine (XII). We now find that the 5-phenoxy group, in this compound, is as firmly bound as that in 5-phenoxyuracil On the other hand, the aliphatic grouping —$CH_2OC_6H_5$ in position 4 undergoes hydrolysis by the action of hydrochloric acid and the diphenoxypyrimidine (XII) is transformed into the chloropyrimidine (XV) with formation of carbolic acid. An attempt to effect an analogous change with the dinaphthoxypyrimidine (XVII) was unsuccessful and only amorphous products of indefinite composition were obtained. Since the methyl groups in thymine and 4-methyluracil are not attacked by the halogens, therefore this reaction is of particular interest and we hope to be able to apply it later and synthesize the unknown chloro derivatives, (VII and VIII), of these two pyrimidines. These halides should be of value for further interesting syntheses.

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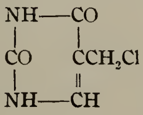
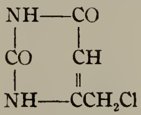
[1] We shall describe in a future paper the results of our investigation on catalysis in Claisen's condensation.—T. B. J.

[2] J. Biol. Chem., **1**, 437.

[3] This Journal, **42**, 272.

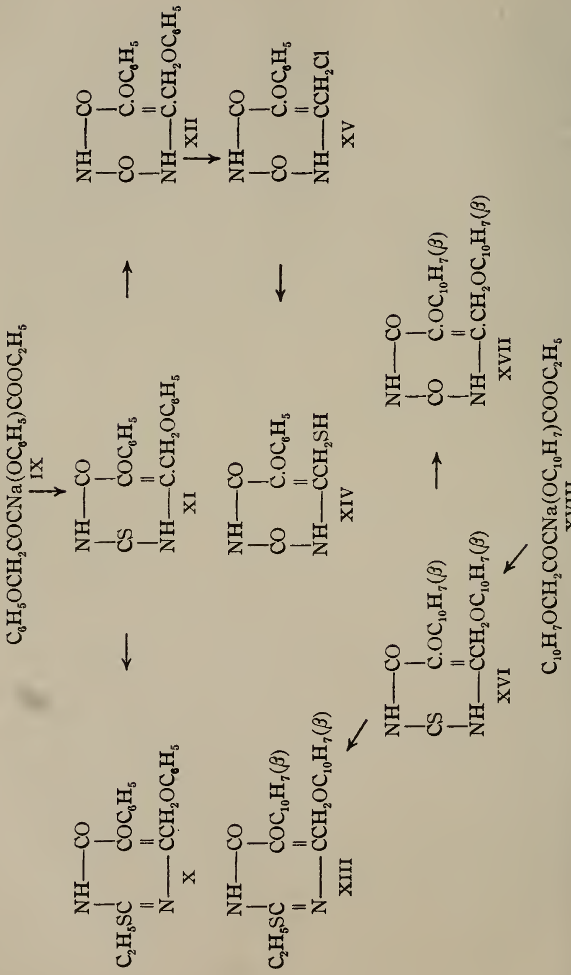


VII

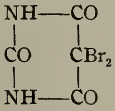


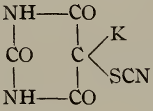
VIII

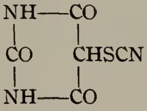
We have now made the interesting observation that this chloropyrimidine (XV), which contains the same unsaturated grouping as is present in allyl chloride, —C : $C.CH_2Cl$, reacts with potassium thiocyanate in an abnormal manner. The product of the reaction is neither a thiocyanate nor an isothiocyanate, but the mercaptopyrimidine (XIV). The thiocyanate is apparently the primary product of the reaction, but, instead of rearranging to an isothiocyanate, it loses its cyanogen radical and a mercaptan is formed. So far as the writer is aware this is the first case where it has been observed that a primary halide can react with potassium thiocyanate, in an alcoholic solution, in this unique manner with formation of a mercaptan. It is especially interesting that we should observe this behavior with a halide containing a grouping favorable for the formation of an isothiocyanate. These various transformations are represented by the following formulas:

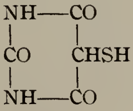

IX
X
XI
XII
XIII
XIV
XV
XVI
XVII
XVIII

Regarding the mechanism of this unique change, we have no decisive evidence, but it is apparently analogous to that involved in the transformation of thiocyanobarbituric acid (XXI) into thiodialuric acid (XXII). Trzcinski[1] prepared the potassium salt of this interesting thiocyanate (XX) by the action of potassium thiocyanate on dibromobarbituric acid (XIX), but he was unable to isolate the free thiocyanate because of its instability. He writes as follows regarding the properties of this thiocyanate: "Vermischt man concentrirte Lösungen ihrer Salze mit überschüssiger Salzsäure, so entsteht ein krystallinischer, in Wasser löslicher Niederschlag, der sich aber nicht unkrystallisiren lässt, indem er, schon gelinde mit Wasser erwärmt, sich zersetzt, wobei Sulfodialursäure, Blausäure, Sulfocyansäure und ein in Alkalien und Säuren unloslicher Körper entstehen."


XIX


XX


XXI


XXII

The study of chloropyrimidines containing the grouping —C : C.CH_2Cl will be continued.

EXPERIMENTAL PART

Sodium Salt of Ethyl α,γ-Diphenoxyacetoacetate, $C_6H_5OCH_2COCNa(OC_6H_5)COOC_2H_5$—This salt was obtained by the molecular condensation of ethyl phenoxyacetate in ether solution and in presence of the required amount of metallic sodium. The sodium gradually dissolved and the salt deposited as a light colored granular powder. The yield of salt from 25 grams of ethyl phenoxyacetate was 18 grams. This crude salt was used for the preparation of

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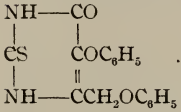
[1] Ber. d. chem. Ges., **16**, 1060.

2-Thio-4-phenoxymethyl-5-phenoxy-6-oxypyrimidine,

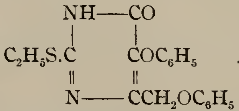


$$\begin{array}{lll} \mathrm{NH} & — & \mathrm{CO} \\ | & & | \\ \mathrm{CS} & & \mathrm{COC_6H_5} \\ | & & \| \\ \mathrm{NH} & — & \mathrm{CCH_2OC_6H_5} \end{array}$$

.—Calculating that the sodium salt (18 grams) was pure, molecular proportions of sodium and thiourea were dissolved in absolute alcohol and the sodium salt suspended in the solution. After heating on the steam bath for about 10 hours the condensation was considered complete and the excess of alcohol evaporated. The residue was then dissolved in a small volume of water and hydrochloric acid added cautiously, when hydrogen sulphide was evolved and this pyrimidine separated in a crystalline condition. Sometimes the product was oily and slowly hardened on cooling. It was purified by crystallization from alcohol. The pyrimidine is soluble in alcohol and benzene and difficultly soluble in water. It crystallizes from alcohol in slender prisms, which melt at 218° to a red oil. The yield was 8 grams. Analysis (Kjeldahl):

	Calculated for $C_{17}H_{14}O_3N_2S$	Found
N	8.58	8.30

2-Ethylmercapto-4-phenoxymethyl-5-phenoxy-6-oxypyrimidine,



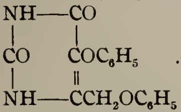
$$\begin{array}{rcl} \mathrm{NH} & — & \mathrm{CO} \\ | & & | \\ \mathrm{C_2H_5S.C} & & \mathrm{COC_6H_5} \\ \| & & \| \\ \mathrm{N} & — & \mathrm{CCH_2OC_6H_5} \end{array}$$

.—Six-tenths of a gram of sodium was dissolved in alcohol and 8 grams of the preceding 2-thiopyrimidine dissolved in the solution by warming on the steam bath. Six and five-tenths grams of ethyl iodide were then added and the solution heated for about 30 minutes at 100°, when it was neutral. The alcohol and excess of iodide were then evaporated and the crude mercaptopyrimidine triturated with water to remove sodium iodide. The pyrimidine was purified by crystallization from alcohol and melted at 170°. It crystallizes in characteristic, hexagonal prisms, which are insoluble in water and quite soluble in benzene. Analyses (Kjeldahl):

	Calculated for $C_{19}H_{18}O_3N_2S$	Found I	Found II
N	7.90	7.74	7.86

Attempts to hydrolyze this mercaptopyrimidine to 2,6-dioxy-4-phenoxymethyl-5-phenoxypyrimidine were unsuccessful. It was recovered unaltered after long digestion with hydrochloric and hydrobromic acids.

2,6-Dioxy-4-phenoxymethyl-5-phenoxypyrimidine,

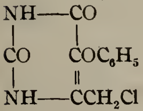


$$\begin{array}{lcl} NH & - & CO \\ | & & | \\ CO & & COC_6H_5 \\ | & & \| \\ NH & - & CCH_2OC_6H_5 \end{array}$$

.—This pyrimidine was formed by digesting the corresponding 2-thiopyrimidine with a strong aqueous solution of chloroacetic acid. The thio compound dissolved on boiling and finally, when the desulphurization was complete, this pyrimidine separated from the hot solution in a crystalline condition. It is soluble in benzene and alcohol and insoluble in water. It crystallizes from alcohol in distorted needles or hairs, which melt at 200°. It did not contain sulphur. Analyses (Kjeldahl):

	Calculated for $C_{17}H_{14}O_4N_2$	Found I	Found II
N	9.03	9.15	9.15

2,6-Dioxy-4-chloromethyl-5-phenoxypyrimidine,

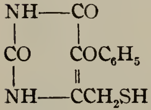


$$\begin{array}{lcl} NH & - & CO \\ | & & | \\ CO & & COC_6H_5 \\ | & & \| \\ NH & - & CCH_2Cl \end{array}$$

.—This pyrimidine was obtained by heating the above diphenoxypyrimidine with hydrochloric acid. The transformation, however, is not smooth and considerable resinous material is formed during the reaction. After several preliminary experiments it was finally found that the best yield of chloropyrimidine was obtained under the following conditions: Five grams of 2,6-dioxy-4-phenoxymethyl-5-phenoxypyrimidine were heated with 25 cc. of concentrated hydrochloric acid, in a bomb tube, for 5 hours, at 140°–150°. A dark solution was obtained and some resinous substance was suspended in the fluid. The contents of the tube were evaporated on the steam bath when a resinous residue was obtained. We then triturated this with warm water, when it finally congealed to an amorphous product, which was soluble in warm alcohol. On cooling, this chloropyrimidine separated in characteristic, square plates, which melted at 248°. It gave a strong test for chlorine. The compound is soluble in alcohol and hot water and insoluble in benzene. Analyses (Kjeldahl):

	Calculated for $C_{11}H_9O_3N_2Cl$	Found I	Found II
N	11.09	11.05	11.02

2,6-Dioxy-4-mercaptomethyl-5-phenoxypyrimidine,



.—Two grams of 2,6-dioxy-4-chloromethyl-5-phenoxypyrimidine and one gram of dry potassium thiocyanate were dissolved in alcohol and the solution heated on the steam bath for 5–6 hours. Potassium chloride deposited on the sides of the flask. The solution was evaporated to remove all alcohol, when we obtained an oil which finally solidified on cooling. After trituration with water to dissolve potassium chloride and potassium thiocyanate the compound was purified by crystallization from alcohol. It separated from this solvent in needles, which decomposed at 182°. This decomposition point is very characteristic. The compound shrivels abruptly, forming a resin, at 182°, and then decomposes as the temperature is raised. It gave a strong test for sulphur. Analyses:

Nitrogen determination (Kjeldahl).

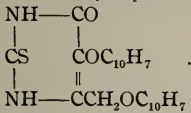
Sulphur determination (Carius).

I. 0.1468 gram substance gave 0.1329 gram $BaSO_4$.

	Calculated for $C_{11}H_{10}O_3N_2S$	Found I	Found II	Found III
N	11.2	10.65	11.12	. . .
S	12.8	. . .	. . .	12.43

Sodium Salt of Ethyl α,α-Dinaphthoxyacetoacetate, $C_{10}H_7OCH_2COCNa(OC_{10}H_7)COOC_2H_5$.—This salt was obtained by the molecular condensation of ethyl β-naphthoxyacetate[1] in the presence of the required amount of sodium. The salt was obtained as a granular powder but the yield was poorer than in the case of the corresponding phenoxy derivative. No attempt was made to isolate the ketone ester and we used the crude salt for the preparation of the following pyrimidine:

2-Thio-4-naphthoxymethyl-5-naphthoxy-6-oxypyrimidine,

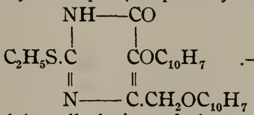


$$\begin{array}{lll} NH & — & CO \\ | & & | \\ CS & & COC_{10}H_7 \\ | & & \| \\ NH & — & CCH_2OC_{10}H_7 \end{array}$$

.—Sixty-five hundredths of a gram of sodium was dissolved in absolute alcohol and 12.8 grams of the crude sodium salt (above) and 3.2 grams of thiourea suspended in the solution. The mixture was then heated at 100° for ten hours and the alcohol evaporated. The residue was dissolved in the smallest volume of water possible and the solution acidified with hydrochloric acid. Hydrogen sulphide was evolved and this thiopyrimidine separated. The compound is insoluble in water and difficultly soluble in alcohol. It crystallizes from hot alcohol in characteristic, rhombic tables or plates, which melt at 224°–226° to a red oil. Analysis (Kjeldahl):

	Calculated for $C_{25}H_{18}O_3N_2S$	Found
N	6.57	6.54

2-Ethylmercapto-4-naphthoxymethyl-5-naphthoxy-6-oxypyrimidine,



$$\begin{array}{lll} & NH & — & CO \\ & | & & | \\ C_2H_5S.C & & & COC_{10}H_7 \\ & \| & & \| \\ & N & — & C.CH_2OC_{10}H_7 \end{array}$$

.—This mercaptopyrimidine was formed by alkylation of the preceding 2-thiopyrimidine with ethyl bromide in the presence of sodium ethylate. It is insoluble in water and soluble in benzene and alcohol. It was purified by crystallization from alcohol and crystallized in sheaves of needles melting at 198°. The mercapto group is not removed by digestion with concentrated hydrochloric or hydrobromic acid. Analysis (Kjeldahl):

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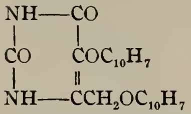
[1] *Loc. cit.*

	Calculated for $C_{27}H_{22}O_3N_2S$	Found
N	6.16	6.30

2,6-Dioxy-4-naphthoxymethyl-5-naphthoxypyrimidine,



.—Five grams of 2-thio-4-naphthoxymethyl-5-naphthoxy-6-oxypyrimidine were suspended in a concentrated aqueous solution of chloroacetic acid and the mixture heated to boiling for 7 hours. The thiopyrimidine finally completely dissolved and then this desulphurized product separated from the hot solution. The yield was quantitative. The pyrimidine was purified by crystallization from absolute alcohol and separated in minute needles arranged in clusters. Oftentimes it deposited in an amorphous state resembling freshly precipitated aluminium hydroxide. It was free from sulphur and melted at 256°–258° to a red oil. It is insoluble in water and benzene. Analysis (Kjeldahl):

	Calculated for $C_{25}H_{18}O_4N_2$	Found
N	6.83	7.09

Attempts to convert this dinaphthoxypyrimidine into 2,6-dioxy-4-chloromethyl-5-naphthoxypyrimidine were unsuccessful. It was heated with concentrated hydrochloric acid at different temperatures, but in every case products of a tarry nature were obtained and a pure chloro compound could not be isolated. Nitrogen and chlorine determinations in the purest product obtainable gave 6.9 per cent. for nitrogen and 1.5 per cent. for chlorine, while the calculated values for the pure chloropyrimidine are 9.2 per cent. and 11.2 per cent., respectively.

New Haven, Conn.
July 1, 1912

[Contributions from the Sheffield Laboratory of Yale University]

CCIV.—RESEARCHES ON PYRIMIDINES

THE OXIMES OF SOME THIOGLYCOLLIDE COMPOUNDS AND THEIR BEHAVIOR ON REDUCTION[1]

By Treat B. Johnson and Robert C. Moran

[FIFTY-EIGHTH PAPER]

In a preceding publication from this laboratory,[2] Johnson and Shepard have described a synthesis of the oxime of mercaptopyruvic acid or α-oximido-β-mercaptopropionic acid (IV). It was obtained by the action of hydroxylamine on 4-methyl-6-oxypyrimidine-2-oxalothioglycollic acid (I) or 4-methyl-6-oxypyrimidine-2-thiopyruvic acid (III). The product of the reaction, in both cases, was the oxime of the pyruvic acid (II), which then reacted with an excess of the hydroxylamine, forming the oxime of mercaptopyruvic acid (IV) and 2-oximido-4-methyl-6-oxypyrimidine (V). The various changes involved in this synthesis are represented by the following formulas.

These two oximes, (IV) and (II), represent new types of sulphur compounds and naturally were of interest to us because of the possibility of their conversion, by reduction, into the corresponding amino acids. All attempts, however, to effect this change were unsuccessful. We found, on the other hand, that these two acids were extremely unstable in the presence of reducing agents and underwent partial hydrolysis with regeneration of hydroxylamine. The oximido groups were likewise reduced as expected, but, much to our surprise, the sulphur was also detached from the aliphatic residue with formation of alanine (VII), hydrogen sulphide and 2-thio-4-methyl-6-oxypyrimidine (IX). In other words, we obtained

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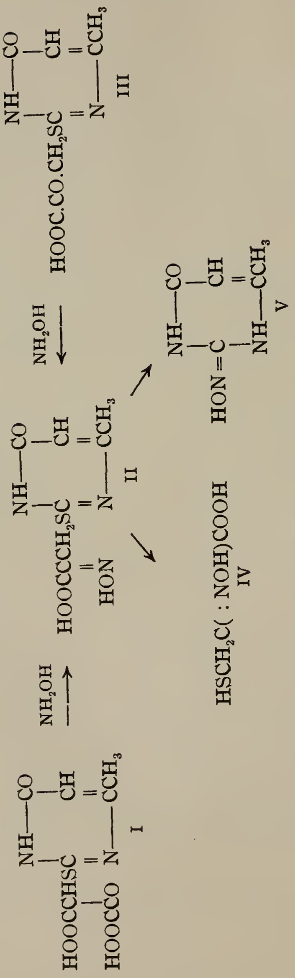
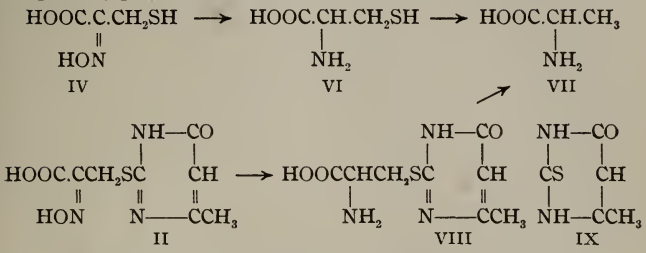
[1] By the terms *thioglycollide* and *glycollide* are meant the groupings —$S.CH_2.CO$— and —$O.CH_2.CO$—, respectively, corresponding to the *polypeptide* grouping —$NH.CH_2.CO$—.—T. B. J.

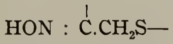
[2] This Journal, **48,** 279.


I
NH₂OH
II
NH₂OH
III
IV
V

no evidence of the formation of cysteine (VI) or the corresponding pyrimidine derivative (VIII).



The behavior of these oximido acids on reduction was so unexpected and unique that it was of interest to examine another series of oximes containing the grouping



$$HON : \overset{|}{C}.CH_2S—$$

It was desirable to determine whether it is a characteristic property of compounds containing this linking to undergo reduction in this manner, or whether this behavior is due, in this case, to the presence of the carboxyl group of the oximido acid. In this paper we shall describe some representatives of a class of oximes containing the same grouping, but in which the carboxyl group of the above oximido acids is replaced by an aryl or alkyl group.

In the present investigation the starting point was 2-thio-4-methyl-6-oxypyrimidine.[1] This was converted into its sodium salt (X) and the latter then digested with monochloroacetone and bromoacetophenone, when the two pyrimidines, 2-acetylmethylmercapto-4-methyl-6-oxypyrimidine (XI) and 2-benzoylmethylmercapto-4-methyl-6-oxypyrimidine (XII), respectively, were obtained in excellent yields. Both of these ketones reacted smoothly with hydroxylamine, forming the corresponding oximes, (XIII) and (XV), respectively. We did not observe the formation of stereoisomeric modifications. We also prepared the hydrazone of 2-benzoylmethylmercapto-4-methyl-6-oxypyrimidine (XIV).

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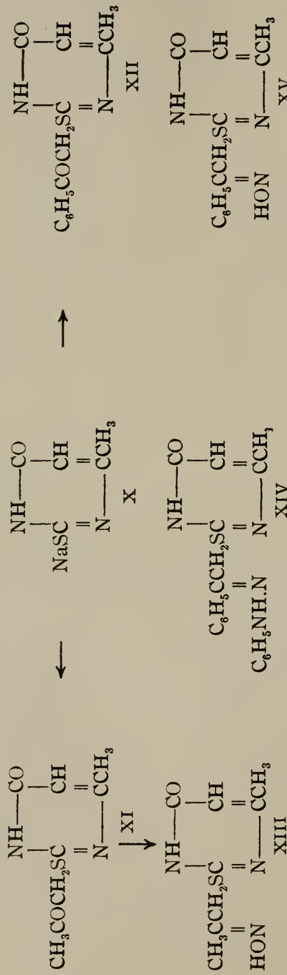
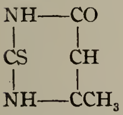
[1] List: Ann. Chem. (Liebig), **236**, 12.

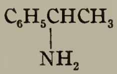

X
XI
XII
XIII
XIV
XV
NaSC
CH₃COCH₂SC
C₆H₅COCH₂SC
CH₃CCH₂SC
HON
C₆H₅CCH₂SC
C₆H₅NH.N
NH—CO
CH
N—CCH₃

We have examined the behavior, towards reducing agents, of the oxime (XV) and hydrazone (XIV) of 2-benzoylmethylmercapto-4-methyl-6-oxypyrimidine. The oxime was reduced with ferrous sulphate and ammonia, with formic acid and zinc dust and with sodium amalgam. In every case we obtained 2-thio-4-methyl-6-oxypyrimidine (XVI). In the experiment in which sodium amalgam was used, we also succeeded in isolating phenylethylamine (XVII). This combined with phenyl isothiocyanate, giving methyldiphenylthiourea (XIX), which has been described by Michaelis and Linow.[1] We obtained no evidence of the formation of the amine (XVIII). Attempts to prepare this amine by reduction of the hydrazone (XIV) with sodium amalgam and aluminium amalgam were likewise unsuccessful. The only product which was identified was 2-thio-4-methyl-6-oxypyrimidine (XVI). The ketone (XII) was reduced by aluminium amalgam, in an alcoholic solution, forming 2-thio-4-methyl-6-oxypyrimidine (XVI) and apparently acetophenone.



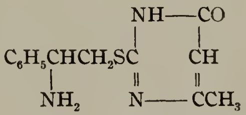
$$\begin{array}{ll} NH & \!\!—CO \\ | & | \\ CS & CH \\ | & | \\ NH & \!\!—CCH_3 \end{array}$$

XVI



$$\begin{array}{c} C_6H_5CHCH_3 \\ | \\ NH_2 \end{array}$$

XVII



$$\begin{array}{lll} & NH & \!\!—CO \\ & | & | \\ C_6H_5CHCH_2SC & & CH \\ | & \| & \| \\ NH_2 & N & \!\!—CCH_3 \end{array}$$

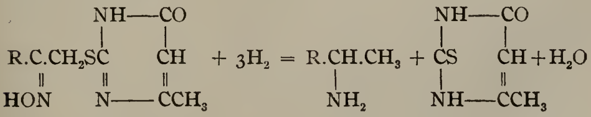
XVIII

$C_6H_5NHCSNHCH(CH_3)C_6H_5$

XIX

Summary

Oximes of the general formula (XX) ($R = CH_3$, C_6H_5, COOH) are converted by reducing agents into amines and 2-thiopyrimidines.



$$\begin{array}{llll} & NH & \!\!—CO & \\ & | & | & \\ R.C.CH_2SC & & CH & + 3H_2 = \\ \| & \| & \| & \\ HON & N & \!\!—CCH_3 & \end{array} \begin{array}{lll} & NH & \!\!—CO \\ & | & | \\ R.CH.CH_3 + & CS & CH + H_2O \\ | & | & \| \\ NH_2 & NH & \!\!—CCH_3 \end{array}$$

XX

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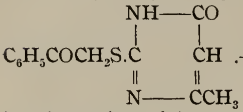
[1] Ber. d. chem. Ges., 26, 2168.

EXPERIMENTAL PART

2-Benzoylmethylmercapto-4-methyl-6-oxypyrimidine,



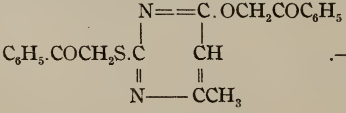
$$\begin{array}{rccl} & \mathrm{NH} & — & \mathrm{CO} \\ & | & & | \\ C_6H_5COCH_2S. & C & & CH \\ & \| & & \| \\ & N & — & CCH_3 \end{array}$$

.—This pyrimidine is formed smoothly by the action of bromoacetophenone on the sodium salt of 2-thio-4-methyluracil. The dry sodium salt (20 grams) was suspended in 100 cc. of absolute alcohol and one molecular proportion of the bromide added (24.3 grams). On warming on the steam bath, there was an immediate reaction, the sodium salt dissolved and sodium bromide deposited. After digesting for about 3 hours the reaction was complete and the solution was neutral to turmeric and litmus. The solution was then cooled, when the above pyrimidine separated in well developed prisms mixed with sodium bromide. The pyrimidine was purified by first washing with cold water to remove sodium bromide and by recrystallization from alcohol. It crystallized, on cooling, in colorless prismatic crystals, which melted at 175° to an oil without decomposition. The yield of pure pyrimidine was 19.1 grams. The pyrimidine is soluble in dilute sodium hydroxide solution and insoluble in water. Analysis (Kjeldahl):

	Calculated for $C_{13}H_{12}O_2N_2S$	Found
N	10.72	10.70

After filtering from the mercaptopyrimidine the alcohol filtrate (above) was concentrated on the steam bath, when we obtained a syrupy residue, which deposited crystals on cooling. This product was separated and purified by recrystallization from hot alcohol. It was more soluble in alcohol than the pyrimidine and separated, on cooling, in prisms which melted at 118°–119° to a clear oil without effervescence. It was identified as

2-Benzoylmethylmercapto-4-methyl-6-benzoylmethoxypyrimidine,



$$\begin{array}{rccl} & N & = & C.OCH_2COC_6H_5 \\ & | & & | \\ C_6H_5.COCH_2S. & C & & CH \\ & \| & & \| \\ & N & — & CCH_3 \end{array}$$

.—This same compound was also obtained by digesting, in alcohol, the sodium salt of 2-benzoylmethylmercapto-4-methyl-6-oxypyrimidine (see below) with the required amount of bromoacetophenone. The compound is formed smoothly in this manner and after concentration of the alcohol solution it separated in beautiful, prismatic crystals, which melted at 118°–119° to a clear oil. The constitution of the pyrimidine is established by the facts that it is not soluble in sodium hydroxide solution and is converted into 2-benzoylmethylmercapto-4-methyl-6-oxypyrimidine by hydrolysis with acids. Analysis (Kjeldahl):

	Calculated for $C_{21}H_{18}O_3N_2S$	Found
N	7.40	7.40

Hydrolysis with Hydrochloric Acid.—One gram of the above pyrimidine was suspended in 60 cc. of concentrated hydrochloric acid and the mixture heated on the steam bath for just 10 minutes. We obtained a colorless solution which deposited, on cooling, a colorless crystalline substance. This was purified by crystallization from alcohol and separated in prisms, which melted at 175°. They contained sulphur and were identified as 2-benzoylmethylmercapto-4-methyl-6-oxypyrimidine. The latter pyrimidine on prolonged hydrolysis is finally converted into 4-methyluracil. For example: Two grams of the pyrimidine were suspended in 50 cc. of concentrated hydrochloric acid and the mixture boiled for about 1.5–2 hours. An oil was obtained, which solidified on cooling. This was separated and recrystallized from boiling alcohol. It separated, on cooling, in yellow prisms, which melted at 115° to an oil without decomposition. The substance gave a strong test for sulphur, but did not contain nitrogen. When some of the compound was placed in concentrated sulphuric acid it dissolved, giving a brilliant purple solution. This color was destroyed by dilution with water. The compound was not desulphurized by digestion in dilute alcoholic solution with silver nitrate, mercury oxide or lead acetate. Apparently this compound was not the mercaptan $C_6H_5COCH_2SH$ or its corresponding disulphide, $(C_6H_5COCH_2S)_2$. It is now being investigated and the results obtained will be published in a later paper. Sulphur determination (Kjeldahl):

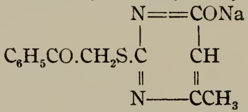
I. 0.3004 gram substance gave 0.07333 gram $BaSO_4$.

	Calculated for C_8H_8OS	Found
S	20.3	24.4

The acid filtrate (above) was evaporated to dryness and the residue dissolved in a small volume of hot water. On cooling methyluracil deposited. Analysis (Kjeldahl):

	Calculated for $C_5H_6O_2N_2$	Found
N	22.22	22.37

Sodium Salt of 2-Benzoylmethylmercapto-4-methyl-6-oxypyrimidine,

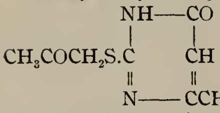


$$\begin{array}{rll} & \mathrm{N} = & \mathrm{CONa} \\ & | & | \\ \mathrm{C_6H_5CO.CH_2S.C} & & \mathrm{CH} \\ & \| & \| \\ & \mathrm{N} - & \mathrm{CCH_3} \end{array}$$

.—Sixty-three hundredths of a gram of pure sodium hydroxide was dissolved in 15 cc. of cold water and 2 grams of the mercaptopyrimidine dissolved in the solution by gentle warming. On cooling, this salt separated in the form of needles. The compound shrivels when heated, in a capillary tube, above 100° and decomposes at 206° with effervescence. The weight of salt which separated was 1.9 grams. Analysis (Kjeldahl):

	Calculated for $C_{13}H_{11}O_2N_2SNa$	Found
N	9.93	9.90

2-Acetylmethylmercapto-4-methyl-6-oxypyrimidine,

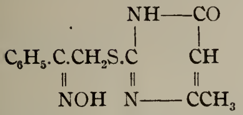


$$\begin{array}{rll} & \mathrm{NH} - & \mathrm{CO} \\ & | & | \\ \mathrm{CH_3COCH_2S.C} & & \mathrm{CH} \\ & \| & \| \\ & \mathrm{N} - & \mathrm{CCH_3} \end{array}$$

.—This pyrimidine was prepared by digestion of the sodium salt of 2-thio-4-methyluracil in alcohol with the required amount of chloroacetone. It was purified by recrystallization from hot alcohol and separated, on cooling, in slender needlelike prisms, which melted at 152° to a clear oil without decomposition. The pyrimidine is insoluble in hot and cold water and soluble in sodium hydroxide solution. Analysis (Kjeldahl):

	Calculated for $C_8H_{10}O_2N_2S$	Found
N	14.14	14.4

Oxime of 2-Benzoylmethylmercapto-4-methyl-6-oxypyrimidine,



$$\begin{array}{lcl} & \mathrm{NH}-\!\!- & \mathrm{CO} \\ & | & | \\ \mathrm{C_6H_5.C.CH_2S.C} & & \mathrm{CH} \\ \quad\ \| \qquad\quad \| & & \| \\ \ \mathrm{NOH}\quad \mathrm{N}-\!\!-\!\!- & & \mathrm{CCH_3} \end{array}$$

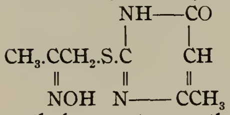
.—This oxime was prepared by the action of hydroxylamine on 2-benzoylmethylmercapto-4-methyl-6-oxypyrimidine in aqueous solution. Four grams of the pyrimidine and 1.23 grams of sodium hydroxide were dissolved in 25 cc. of water. To this cold solution were then added 1.07 grams of hydroxylamine hydrochloride dissolved in 5 cc. of water. The mixture was then allowed to stand at ordinary temperature for 10–12 hours when it had assumed a pale yellow color and a small amount of solid material had separated. This was separated by filtration and sufficient hydrochloric acid added to the filtrate to combine with the sodium. A slight amount of hydrogen sulphide was evolved and the oxime separated as a light yellow solid. It was dried in a desiccator over concentrated sulphuric acid. It was purified for analysis by recrystallization from alcohol and melted at 183° to a yellow oil with effervescence. The oxime dissolves in sodium hydroxide solution but is insoluble in water. While the oxime could be recrystallized in small quantities from alcohol, nevertheless attempts to purify large amounts in this manner were unsuccessful. It dissolves with some difficulty and the oxime is partially decomposed by long boiling, forming methyluracil. Analysis (Kjeldahl):

	Calculated for $C_{13}H_{13}O_2N_3S$	Found
N	15.27	15.30

Hydrochloride of the Oxime.—The oxime separated in the form of its hydrochloric acid salt when it was precipitated from its alkaline solution by addition of an excess of hydrochloric acid. Analysis (Kjeldahl):

	Calculated for $C_{13}H_{13}O_2N_3S.HCl$	Found
N	13.48	13.31

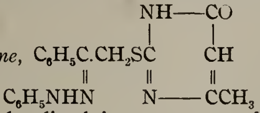
Oxime of 2-Acetylmethylmercapto-4-methyl-6-oxypyrimidine,



.—While the oxime of 2-benzoylmethylmercapto-4-methyl-6-oxypyrimidine was formed in aqueous solution this oxime, on the other hand, did not form smoothly under similar conditions. It was therefore prepared as follows: The pyrimidine was dissolved in alcohol and this solution combined with an aqueous solution containing the required amount of hydroxylamine. On standing at ordinary temperature the oxime finally separated as a colorless solid. It was difficultly soluble in alcohol and was decomposed by warming with water, forming 2-acetylmethylmercapto-4-methyl-6-oxypyrimidine melting at 152°. The oxime melts at about 162° to an oil with decomposition. Analysis (Kjeldahl):

	Calculated for $C_8H_{11}O_2N_3S$	Found
N	19.71	19.3

Reduction of 2-Benzoylmethylmercapto-4-methyl-6-oxypyrimidine with Aluminium Amalgam.—Five grams of the pyrimidine were dissolved in 95 per cent. alcohol and about 10 grams of amalgamated aluminium suspended in the solution. The reduction was conducted in a flask and the latter was connected with a return condenser. The reaction was allowed to proceed for 10–12 hours when 5 cc. of water were added and the mixture then heated on the steam bath for 2 hours. The mixture was then cooled, the aluminium hydroxide and excess of amalgam separated by filtration and the alcohol filtrate concentrated on the steam bath. On cooling, a crystalline substance separated. This gave a strong test for sulphur and was identified as 2-thio-4-methyluracil. The alcohol filtrate was concentrated still further and cooled again when the unaltered mercaptopyrimidine separated and melted at 175°.

Phenylhydrazone of 2-Benzoylmethylmercapto-4-methyl-6-oxypyrimidine, 

$$\begin{array}{rccc} & \text{NH} & — & \text{CO} \\ & | & & | \\ \text{C}_6\text{H}_5\text{C.CH}_2\text{S} & \text{C} & & \text{CH} \\ \| & \| & & \| \\ \text{C}_6\text{H}_5\text{NHN} & \text{N} & — & \text{CCH}_3 \end{array}$$

.—This hydrazone was prepared by dissolving 2.5 grams of phenylhydrazine in 5 cc. of alcohol and then adding the solution to an alcoholic solution of the mercaptopyrimidine. Within a few minutes the hydrazone began to separate and after 10 minutes the reaction was apparently complete. The hydrazone is difficultly soluble in boiling alcohol, insoluble in water and soluble in dilute sodium hydroxide solution. It crystallizes in needles, which melt at about 295° to a dark oil. Analysis (Kjeldahl):

	Calculated for $C_{19}H_{18}ON_4S$	Found
N	16.00	15.95

Especially interesting was the behavior of phenylhydrazine towards 2-benzoylmethylmercapto-4-methyl-6-oxypyrimidine in glacial acetic acid solution. Five grams of the mercaptopyrimidine were dissolved in cold glacial acetic acid and 2.1 grams of phenylhydrazine added to the solution. There was no evidence of any reaction and the mixture was heated at 100° for about 2 hours. On cooling, a crystalline substance separated. This contained sulphur but did not melt below 300°. It was identified as 2-thio-4-methyluracil. Analysis (Kjeldahl);

	Calculated for $C_5H_6ON_2S$	Found
N	19.72	19.71

Reduction of the Hydrazone with Sodium Amalgam.—In this experiment 5 grams of the hydrazone and 15 grams of 3 per cent. amalgam were suspended in 75 cc. of alcohol and the reduction continued for about 12 hours at ordinary temperature. Eleven grams of amalgam were then added and the mixture allowed to stand for 12 hours. The greater part of the hydrazone had then dissolved and an insoluble gray product was suspended in the alcohol. There was only a small amount of this, however, and it was not examined. After filtering, the red filtrate was acidified with hydrochloric acid, the sodium chloride separated by filtration and the solution then evaporated to dryness. We obtained a dark oily residue, which partially solidified after warming with water and cooling. The oil was extracted with ether and the aqueous solution evaporated, when we obtained, on cooling, 2-thio-4-methyluracil. Not enough material was dissolved by the ether for identification.

Reduction with Aluminium Amalgam.—In this experiment 4 grams of the hydrazone and an excess of amalgamated aluminium were suspended in a mixture of 300 cc. of alcohol and 50 cc. of water and this then warmed on the steam bath for 5 hours. Hydrogen sulphide was slowly evolved by this treatment. The mixture was finally filtered and the alcohol filtrate concentrated to a volume of about 10–15 cc., when 2-thio-4-methyluracil began to deposit in the form of needle-like prisms. On cooling, a small amount of oil also separated. No definite product was identified, however, except this thiopyrimidine. Analysis (Kjeldahl):

	Calculated for $C_5H_6ON_2S$	Found
N	19.72	19.70

Reduction of the Oxime of 2-Benzoylmethylmercapto-4-methyl-6-oxypyrimidine

With Sodium Amalgam.—Twelve and five-tenths grams of the oxime and an excess of amalgam (3 per cent.) were suspended in 100 cc. of 95 per cent. alcohol and the mixture then heated for one hour on the steam bath and allowed to stand for 10–12 hours at ordinary temperature. Ammonia was evolved during the heating. We obtained a yellow solution. This was acidified with hydrochloric acid, when a crystalline substance deposited mixed with sodium chloride. This solid was separated and purified by crystallization from hot water. It separated on cooling in slender prisms and was identified as 2-thio-4-methyluracil. Analysis (Kjeldahl):

	Calculated for $C_5H_6ON_2S$	Found
N	19.72	19.50

The alcohol filtrate (above) was evaporated to dryness, when more of the pyrimidine separated mixed with a basic oil. This mixture was then triturated with dilute sodium hydroxide to dissolve the pyrimidine and the oil extracted with ether and this finally dried over potash. After removal of the ether we obtained a dark red oil which we combined, without further attempts at purification, with phenyl isothiocyanate. They reacted immediately with evolution of heat, and a thick oil was obtained. After warming for a few minutes at 100° to complete the reaction the substance was then dissolved in a small volume of alcohol and the solution cooled. Prismatic crystals finally separated and melted after two crystallizations at 103°–105° to a clear oil. We did not obtain enough of this compound for analysis but it agreed in all its properties with the thiourea,

$$C_6H_5CH(CH_3).NH.CSNHC_6H_5$$[1]

With Ferrous Sulphate and Ammonia.—The oxime (3.5 grams) was dissolved in 100 cc. of dilute aqueous ammonia and combined with a solution of 35.5 grams of iron sulphate dissolved in 100 cc. of water. This mixture was then allowed to stand on the steam oven for about 24 hours, when the reduction was apparently complete. The iron oxide was then separated by filtration and the filtrate concentrated. The only products identified in this solution were ammonium sulphate and 2-thio-4-methyluracil. Therefore the oxime was reduced by ferrous sulphate in the same manner as by the amalgam.

With Formic Acid and Zinc Dust.—Eleven grams of the oxime were dissolved in 100 cc. of formic acid (specific gravity 1.12) and 10 grams of zinc dust added slowly to the solution. The temperature of the solution was not allowed to rise above 25°. Hydrogen sulphide was slowly evolved by this mild treatment. After allowing to stand for 2 days the acid was diluted with water and the zinc precipitated as zinc sulphide.

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[1] Michaelis and Linow: Ber. d. chem. Ges., **26**, 2168.

After filtering off the zinc sulphide the filtrate was evaporated, when we obtained, as in the two preceding experiments, 2-thio-4-methyluracil.

New Haven, Conn.
July 1, 1912

A STUDY OF THE CONDUCTIVITY AND DISSOCIATION OF CERTAIN ORGANIC ACIDS AT 35°, 50° AND 65°

By E. P. Wightman and Harry C. Jones

INTRODUCTION

[*This investigation was carried out with the aid of a Grant from the Carnegie Institution of Washington.*]

A fairly comprehensive study of the conductivity and dissociation of a large number of organic acids at temperatures from zero degrees to thirty-five degrees has already been made, and the results published in This Journal.[1] In order to make this work as nearly complete as possible we have taken up the study of some of these same acids at fifty degrees and sixty-five degrees, repeating the work at thirty-five degrees.

It is not necessary to give a historical review of the literature of the subject, since this has already been done in connection with the work at lower temperatures. A summary of the conclusions previously arrived at is as follows:

1. "The temperature coefficients of conductivity, expressed in conductivity units, increase rapidly with dilution, and decrease rapidly with rise in temperature for weak organic acids—when not hydrated. When the acids are hydrated, the temperature coefficients of conductivity are larger, and their increase with dilution and decrease with rise in temperature both take place at a slower rate.

2. "Organic acids with the largest constants also have the largest temperature coefficients of conductivity expressed in conductivity units.

3. "The percentage temperature coefficients of conduc-

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[1] White and Jones: This Journal, **44**, 156 (1910). Wightman and Jones: *Ibid.*, **46**, 56 (1911).

tivity of the organic acids are generally small and of the same order of magnitude, and decrease with rise in temperature and with increase in dilution." The latter part of this statement, concerning the decrease of the percentage coefficients with increasing dilution, has been found to be incorrect and will be spoken of later.

4. "The conductivity of most of the organic acids is a parabolic function of the temperature, as proved by comparing observed values with those calculated from interpolation formulae.

5. "There is no general statement possible concerning the change in dissociation of the organic acids with change in temperature. Maxima occur with several between 25° and 35°, while in other cases maxima are indicated at slightly higher temperatures than those at which measurements were made. The dissociation of several acids decreases regularly from 0°.

6. "The strong organic acids do not obey the Ostwald dilution law, and, therefore, dissociation constants cannot be obtained for them in the ordinary way.

7. "The migration velocities of the anions of organic acids are a function of the number of atoms present in the anion, and μ_∞ values for dibasic acids may be found by means of this principle." More will be said of this farther on.

8. "Most dibasic organic acids dissociate like monobasic acids.

9. "Isomeric acids do not behave similarly as regards change in their dissociation.

10. "The migration velocities of isomeric ions are identical.

11. "The behavior of the organic acids with respect to the change in their dissociation with the temperature is not in accord with the hypothesis of Thomson and Nernst, which connects dissociating power and dielectric constants, or at least the influence of some other factor is suggested."

EXPERIMENTAL

The apparatus used in the present work was, in general, similar to that employed at lower temperatures.

The mother solutions of the acids were made up either in a 500 cc. or in a 250 cc. flask which had been calibrated for 50° in the following manner: The number of grams of water necessary to give 500 cc. of water at 50° was weighed into the flask and this calibrated at 20°. The 200 cc. flasks in which the other solutions were made up (from the mother solution) were all calibrated for 20° at 20°.

In making up a N/32 solution from an N/8 solution, the latter being the mother solution, 50 cc. of this was diluted to 200 cc. This 50 cc. of the original solution was of course too concentrated, but just enough so that when diluted in a 200 cc. flask calibrated at 20° for 20° it would give a solution which, when heated to 50°, would have the proper concentration, N/32.

The thermostats were similar to that used for 35° in the earlier work, except that the one for 50° and 65° was covered with an asbestos board impregnated with paraffin. There were two small holes for the thermometer and stirrer to pass through, and also holes large enough to place the cells in and take them out. Ordinarily these holes were covered with small pieces of asbestos board.

In this way the evaporation from the surface of the water in the thermostat was lessened, and the vapors above the surface were kept at a temperature not much lower than that of the bath itself. In consequence of this arrangement it was easier to keep the cells, both the exposed portion as well as the portion under water, at a more even temperature.

No account of the reagents used is necessary, since they were fully discussed in the previous paper.[1]

The procedure for obtaining the constants for the cells was as similar as possible to that for obtaining the conductivities of the acids. The cells, after having been previously kept at 50° for some time, were filled with the potassium chloride solution and then placed in the 25° bath. As soon as they had come to constant temperature, which usually required from about twenty minutes to a half hour, measurements were made. A second series of readings was made a half hour later.

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[1] This Journal, **46**, 62 (1911).

An important source of error, which must be taken into account in work at higher temperatures, is the solubility of the glass cell. West[1] and Clover[2], working with Jones, have both shown that this factor can be practically eliminated if certain precautions are taken. First, the cells must be thoroughly boiled out. Then they must be filled with pure water and be allowed to stand at a temperature somewhere about half way between the two extremes worked with; that is, about 50°. The cells were filled with fresh water every day, and, when not in use, were always kept at approximately this temperature. After about a week, no appreciable quantity of the glass will dissolve, provided the conditions are kept practically the same.

To test this, conductivity readings were made at 35°, then at 50° and 65°. The cells were then brought back to 35° and the conductivities measured again. It was found that the two 35° measurements agreed well with one another.

Keeping the cells always at an elevated temperature accomplished a twofold purpose; the first being that just mentioned, and, secondly, the expansion and contraction of the glass and platinum is not so great as to produce any appreciable effect on the cell constants and conductivity readings, as would probably be the case if there was any great change in temperature.

Sometimes on heating the cells to 50° and 60°, especially if they were allowed to stand at these higher temperatures for any length of time, a large number of gas bubbles would form on the electrodes. The cells were always shaken thoroughly in such cases, to get rid of the bubbles before making the measurements.

The cells were usually filled almost to the stoppers, since there was then little space left for evaporation and condensation, which might change the concentration of the solution quite appreciably.

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[1] This Journal, **34**, 508 (1905).

[2] *Ibid.*, **43**, 187 (1910).

RESULTS

The determination and use of the μ_∞ values of the sodium salts of the organic acids needs no explanation here.[1] The following table contains these values for 35°, 50° and 65°:

Table I.—μ_∞ Values for Sodium Salts

	35°	50°	65°
Cyanoacetic	105.8	135.6	171.9
Propionic	100.6	132.0	165.8
Levulinic	93.0	121.0	151.0
Hydroxyisobutyric	94.6	126.2	158.3
Isovaleric	95.5	123.0	153.8
Caprylic	95.4	119.4	159.9
Benzilic	88.6	135.6	171.9
o-Chlorobenzoic	93.5	123.0	153.5
o-Nitrobenzoic	95.2	123.8	155.5
m-Nitrobenzoic	95.2	124.4	156.3
p-Nitrobenzoic	95.2	123.0	153.8
1,2,4-Dinitrobenzoic	93.1	121.1	151.8
1,3,5-Dinitrobenzoic	93.3	121.7	152.6
m-Hydroxybenzoic	98.9	128.2	159.8
p-Hydroxybenzoic	98.9	127.4	158.9
1,2,4–Dihydroxybenzoic	95.2	122.6	153.4
p-Sulphamidobenzoic	93.6	123.3	154.4

A complete table of the μ_∞ values from 0° to 65° of all the acids worked with (except dichlorophthalic, tetrachlorophthalic and meconic acids) is as follows:

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[1] This Journal, **46**, 66 (1911).

Table II.—μ_∞ *Values of the Acids*

Acid	μ_∞ 0°	μ_∞ 15°	μ_∞ 25°	μ_∞ 35°	μ_∞ 50°	μ_∞ 65°
Trichloroacetic	224.8	303.9	355.9	406.4	478.5	520.9
Cyanoacetic	227.0	304.5	360.0	410.0	480.6	551.1
Propionic	223.0	...	354.0	405.0	477.0	545.0
Levulinic	220.9	298.2	348.3	396.9	466.0	430.2
Hydroxyisobutyric	222.8	304.1	357.5	407.4	471.2	537.5
Isovaleric	222.0	299.7	350.0	399.5	468.0	533.0
Caprylic	225.1	300.9	350.8	399.8	464.4	539.1
l-Tartaric	221.0	298.8	350.0	399.9	469.3	534.9
Thiodiglycolic	221.6	300.2	351.1	401.0	470.8	537.5
Tricarballylic	219.9	296.7	347.6	396.8	468.0	535.0
Benzilic	218.7	...	344.7	392.9	458.6	519.9
o-Nitrobenzoic	...	...	...	...	468.8	534.7
m-Nitrobenzoic	...	...	...	...	469.4	535.2
p-Nitrobenzoic	222.2	...	349.7	399.8	468.0	533.0
1,2,4-Dinitrobenzoic	220.0	297.3	347.9	396.8	466.1	531.0
1,3,5-Dinitrobenzoic	220.2	297.4	347.4	396.9	466.7	431.8
o-Chlorobenzoic	220.4	301.8	348.7	397.2	468.0	532.7
p-Hydroxybenzoic	223.0	...	353.0	403.0	472.4	538.1
m-Hydroxybenzoic	223.0	...	353.0	403.0	473.2	539.0
1,2,4-Dihydroxybenzoic	222.0	299.8	350.7	399.1	467.6	532.6
p-Sulphamidobenzoic	221.7	299.3	349.8	398.0	468.3	533.6
Benzenesulphonic	228.0	309.0	359.0	410.3	475.3	544.3
p-Toluenesulphonic	210.6	...	332.7	379.3	445.9	503.4
m-Nitrobenzenesulphonic	204.5	...	323.5	369.4	432.6	591.0
1,4,2-Nitrotoluenesulphonic	228.9	...	318.5	362.3	487.5	556.3
Camphoric	218.3	...	344.5	392.5	458.2	519.0

The μ_∞ values of the dibasic acids in the preceding table were found by means of the graphic method, previously described.[1] It can be seen, however, by glancing at the curve which is given below, that this means of determining the μ_∞ values is not as accurate at the higher temperatures as at the lower, because fewer of the values fall on a definite curve.

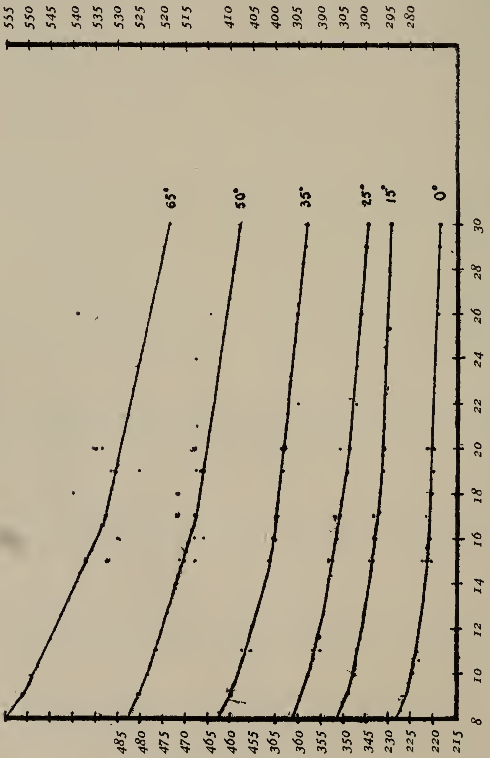

Fig. 1.—Limiting Conductivities

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[1] Wightman and Jones: This Journal, **46**, 69.

The values for the temperature coefficients between 35° and 50° in the following tables were calculated from the values for 35° in the previous paper in almost every case. The figures given for the percentage dissociation and dissociation constants are also taken from the earlier work. The agreement between the values for 35° in the present work and those given before was sufficiently close in most instances to justify this procedure. Where it was not, conductivity measurements were repeated, in which cases the later values were nearly always found to be correct, and so were used in the calculations.

The measurements of the conductivities of *o*-nitrobenzoic, *m*-nitrobenzoic, *m*-hydroxybenzoic and *p*-hydroxybenzoic acids were made by Dr. H. R. Kreider, formerly of this laboratory.

Trichloroacetic Acid

Table III.—Molecular Conductivity

V	35°	50°	65°
8	334.4	388.8	426.6
32	378.7	423.7	465.0
128	389.1	455.1	501.8
512	401.7	476.5	519.5
1024	406.3	478.5	520.9
2048	399.5	473.0	513.4

Table IV.—Temperature Coefficients

	35°–50°		50°–65°	
V	Cond. units	Per cent.	Cond. units	Per cent.
8	3.61	1.08	2.52	0.65
32	4.00	1.10	2.75	0.65
128	4.34	1.11	3.11	0.68
512	4.87	1.21	2.87	0.60
1024	4.80	1.18	2.83	0.59
2048	5.04	1.27	2.69	0.57

Table V.—Percentage Dissociation

V	35°	35°	65°
8	82.34	81.25	81.90
32	89.88	88.55	89.27
128	95.91	95.11	96.33
512	99.26	99.58	99.73
1024	100.00	100.00	100.00

Cyanacetic Acid

Table VI.—Molecular Conductivity

V	35°	50°	65°
8	66.31	74.70	80.43
32	118.8	134.0	144.5
128	199.6	227.8	249.0
512	292.7	337.3	368.0
1024	331.9	381.7	426.9
2048	358.4	418.1	472.6

Table VII.—Temperature Coefficients

	35°–50°		50°–65°	
V	Cond. units	Per cent.	Cond. units	Per cent.
8	0.57	0.87	0.38	0.51
32	1.01	0.85	0.70	0.52
128	1.87	0.93	1.41	0.62
512	2.95	1.01	2.05	0.60
1024	3.31	1.00	3.01	0.79
2048	4.10	1.15	3.63	0.87

Table VIII.—Percentage Dissociation

V	35°	50°	65°
8	16.53	15.55	14.59
32	28.97	27.88	26.22
128	48.70	47.40	45.18
512	71.46	70.18	66.78
1024	80.98	79.42	77.46
2048	86.97	86.99	85.75

Table IX.— Dissociation Constants $\times 10^4$

V	35°	50°	65°
8	39	36	31
32	37	34	29
128	36	33	29
512	35	32	26
1024	34	30	26
2048	28	27	25

Propionic Acid

Table X.—Molecular Conductivity

V	35°	50°	65°
2	1.925	2.195	2.444
8	4.198	4.740	5.231
32	8.415	9.59	10.39
128	16.54	18.88	20.29
512	32.13	36.30	39.23
1024	44.00	50.01	54.25
2048	59.66	67.00	73.66

Table XI.—Temperature Coefficients

	35°–50°		50°–65°	
V	Cond. units	Per cent.	Cond. units	Per cent.
2	0.018	0.93	0.017	0.75
8	0.036	0.86	0.032	0.69
32	0.078	0.93	0.053	0.56
128	0.156	0.94	0.094	0.50
512	0.278	0.87	0.195	0.54
1024	0.401	0.91	0.283	0.57
2048	0.489	0.82	0.444	0.66

Table XII.—Percentage Dissociation

V	35°	50°	65°
2	0.47	0.46	0.45
8	1.04	0.99	0.96
32	2.08	2.01	1.91
128	4.07	3.96	3.72
512	7.93	7.61	7.20
1024	10.87	10.48	9.95
2048	14.88	14.04	13.51

Table XIII.—Dissociation Constants $\times 10^4$

V	35°	50°	65°
2	0.112	0.102	0.101
8	0.137	0.125	0.126
32	0.138	0.129	0.116
128	0.135	0.128	0.113
512	0.134	0.122	0.109
1024	0.130	0.120	0.108
2048	0.127	0.112	0.103

Levulinic Acid

Table XIV.—Molecular Conductivity

V	35°	50°	65°
8	5.636	6.463	7.189
32	11.13	12.96	14.39
128	21.90	25.54	28.38
512	41.78	48.08	51.79
1024	57.04	66.15	72.81
2048	75.98	86.98	95.76

Table XV.—Temperature Coefficients

	35°–50°		50°–65°	
V	Cond. units	Per cent.	Cond. units	Per cent.
8	0.062	1.12	0.048	0.75
32	0.124	1.12	0.095	0.74
128	0.247	1.15	0.189	0.74
512	0.43	1.03	0.247	0.51
1024	0.61	1.07	0.444	0.67
2048	0.70	0.91	0.585	0.67

Table XVI.—Percentage Dissociation

V	35°	50°	65°
8	1.40	1.39	1.36
32	2.80	2.78	2.71
128	5.50	5.48	5.35
512	10.50	10.32	9.77
1024	14.36	14.19	13.73
2048	19.28	18.66	18.06

Table XVII.—Dissociation Constants $\times 10^4$

V	35°	50°	65°
8	0.249	0.244	0.233
32	0.252	0.249	0.237
128	0.250	0.248	0.236
512	0.241	0.232	0.207
1024	0.235	0.229	0.213
2048	0.225	0.209	0.194

Hydroxyisobutyric Acid

Table XVIII.—Molecular Conductivity

v	35°	50°	65°
8	11.53	13.32	14.73
32	23.09	26.84	29.43
128	44.55	51.41	56.78
512	83.32	96.52	106.8
1024	111.5	128.3	141.8
2048	144.0	166.1	181.4

Table XIX.—Temperature Coefficients

	35°–65°		50°–65°	
v	Cond. units	Per cent.	Cond. units	Per cent.
8	0.12	1.00	0.094	0.71
32	0.26	1.13	0.173	0.65
128	0.45	1.01	0.36	0.70
512	0.88	1.06	0.68	0.71
1024	1.11	1.01	0.90	0.70
2048	1.47	1.02	1.02	0.61

Table XX.—Percentage Dissociation

v	35°	50°	65°
8	2.89	2.83	2.72
32	5.74	5.70	5.43
128	11.15	10.91	10.48
512	20.84	20.48	19.71
1024	27.88	27.23	26.17
2048	36.00	35.24	33.48

Table XXI.—Dissociation Constants $\times 10^4$

v	35°	50°	65°
8	1.08	1.03	0.95
32	1.10	1.08	0.98
128	1.09	1.05	0.97
512	1.07	1.03	0.95
1024	1.08	1.00	0.91
2048	0.99	0.94	0.82

Isovaleric Acid

Table XXII.—Molecular Conductivity

V	0°	15°	25°
8	2.573	3.391	3.869
32	5.365	7.061	8.052
128	10.68	14.04	16.01
512	20.52	26.97	30.74
1024	28.28	37.11	42.18
2048	37.16	49.90	56.86

Table XXIII.—Temperature Coefficients

	0°–15°		15°–25°	
V	Cond. units	Per cent.	Cond. units	Per cent.
8	0.055	2.12	0.048	1.41
32	0.113	2.10	0.099	1.40
128	0.224	2.10	0.197	1.40
512	0.430	2.10	0.377	1.40
1024	0.589	2.08	0.507	1.37
2048	0.844	2.28	0.686	1.39

Table XXIV.—Percentage Dissociation

V	0°	15°	25°
8	1.16	1.13	1.11
32	2.42	2.36	2.30
128	4.81	4.69	4.57
512	9.24	9.00	8.78
1024	12.34	12.38	12.05
2048	16.74	16.65	16.25

Table XXV.—Dissociation Constants × 10^4

V	0°	15°	25°
8	0.170	0.162	0.154
32	0.187	0.178	0.169
128	0.189	0.180	0.171
512	0.184	0.180	0.165
1024	0.170	0.171	0.161
2048	0.164	0.162	0.154

Table XXVI.—Molecular Conductivity

V	35°	50°	65°
8	4.392	4.877	5.115
32	8.927	9.89	10.57
128	17.68	19.52	20.94
512	33.71	36.95	39.92
1024	46.33	50.85	53.48
2048	62.55	69.79	72.93

Table XXVII.—Temperature Coefficients

	25°–35°		35°–50°		50°–65°	
V	Cond. units	Per cent.	Cond. units	Per cent.	Cond. units	Per cent.
8	0.052	1.35	0.032	0.74	0.016	0.33
32	0.087	1.07	0.064	0.72	0.045	0.46
128	0.167	1.04	0.123	0.70	0.095	0.49
512	0.297	0.97	0.216	0.64	0.138	0.37
1024	0.415	0.98	0.301	0.65	0.175	0.34
2048	0.569	1.00	0.483	0.77	0.209	0.45

Table XXVIII.—Percentage Dissociation

V	35°	50°	65°
8	1.07	1.04	0.96
32	2.24	2.11	1.98
128	4.43	4.17	3.93
512	8.44	7.90	7.49
1024	11.60	10.87	10.03
2048	15.66	14.91	13.68

Table XXIX.—Dissociation Constants $\times 10^4$

V	35°	50°	65°
8	0.145	0.137	0.116
32	0.160	0.143	0.125
128	0.160	0.142	0.126
512	0.152	0.132	0.119
1024	0.149	0.130	0.109
2048	0.140	0.128	0.101

Caprylic Acid

Table XXX.—Molecular Conductivity

V	35°	50°	65°
512	30.81	34.52	37.53
1024	42.37	47.28	50.57
2048	56.84	63.69	66.26

Table XXXI.—Temperature Coefficients

	35°–50°		50°–65°	
V	Cond. units	Per cent.	Cond. units	Per cent.
512	0.23	0.74	0.201	0.58
1024	0.33	0.78	0.219	0.46
2048	0.45	0.80	0.170	....

Table XXXII.—Percentage Dissociation

V	35°	50°	65°
512	7.80	7.43	6.96
1024	10.64	10.18	9.38
2048	14.29	13.71	12.29

Table XXXIII.—Dissociation Constants × 10^4

V	35°	50°	65°
512	0.129	0.117	0.102
1024	0.124	0.112	0.095
2048	0.116	0.106	0.084

Tartaric Acid

Table XXXIV.—Molecular Conductivity

V	35°	50°	65°
32	68.14	80.62	90.80
128	124.5	145.3	165.4
512	212.9	248.9	280.7
1024	263.1	308.4	348.9
2048	328.5	386.7	434.4

Table XXXV.—Temperature Coefficients

	35°–50°		50°–65°	
V	Cond. units	Per cent.	Cond. units	Per cent.
32	0.86	1.27	0.68	0.84
128	1.45	1.17	1.34	0.92
512	2.40	1.13	2.12	0.85
1024	3.12	1.19	2.70	0.88
2048	4.08	1.26	3.18	0.82

Table XXXVI.—Percentage Dissociation

V	35°	50°	65°
32	16.91	17.18	16.97
128	30.88	30.96	30.92
512	53.25	53.03	52.47
1024	65.40	65.71	65.23
2048	81.38	82.40	81.21

Table XXXVII.—Dissociation Constants $\times 10^4$

V	35°	50°	65°
32	10.8	11.1	11.1
128	10.8	10.8	10.8
512	11.8	11.7	11.3
1024	12.1	12.3	11.9
2048	17.4	18.8	17.1

Thiodiglycolic Acid

Table XXXVIII.—Molecular Conductivity

V	35°	50°	65°
8	28.54	32.50	35.68
32	52.64	60.64	66.48
128	96.25	111.0	122.5
512	168.5	194.9[1]	214.7
1024	216.0	249.8[1]	278.9
2048	275.3	318.0	355.3

Table XXXIX.—Temperature Coefficients

	35°–50°		50°–65°	
V	Cond. units	Per cent.	Cond. units	Per cent.
8	0.29	1.03	0.212	0.65
32	0.57	1.09	0.389	0.64
128	1.00	1.04	0.767	0.69
512	1.67	0.99	1.32	0.68
1024	2.24	1.04	1.94	0.78
2048	2.82	1.03	2.49	0.78

Table XL.—Percentage Dissociation

V	35°	50°	65°
8	7.02	6.90	6.64
32	13.01	12.88	12.37
128	23.94	23.58	22.79
512	42.15	41.40	39.94
1024	53.90	53.06	51.88
2048	68.76	67.54	66.10

Table XLI.—Dissociation Constants $\times 10^4$

V	35°	50°	65°
8	6.63	6.39	5.90
32	6.08	5.95	5.46
128	5.89	5.68	5.26
512	6.00	5.71	5.19
1024	6.16	5.86	4.52
2048	7.39	6.86	6.29

Interpolated values.

Tricarballylic Acid

Table XLII.—Molecular Conductivity

V	35°	50°	65°
8	16.28	19.29	22.09
32	32.33	37.97	42.97
128	62.39	73.72	82.46
512	115.0	135.7	150.2
1024	152.7	180.2	203.1
2048	196.5	230.8	261.6

Table XLIII.—Temperature Coefficients

	35°–50°		50°–65°	
V	Cond. units	Per cent.	Cond. units	Per cent.
8	0.20	1.23	0.187	0.97
32	0.35	1.08	0.333	0.88
128	0.76	1.22	0.583	0.79
512	1.35	1.17	0.97	0.71
1024	1.85	1.21	1.22	0.68
2048	2.28	1.16	2.05	0.89

Table XLIV.—Percentage Dissociation

V	35°	50°	65°
8	4.09	4.12	4.13
32	8.16	8.11	8.03
128	15.09	15.75	15.41
512	29.06	29.00	28.07
1024	38.39	38.50	37.96
2048	49.54	49.31	48.90

Table XLV.—Dissociation Constants $\times 10^4$

V	35°	50°	65°
8	2.18	2.21	2.22
32	2.27	2.24	2.19
128	2.28	2.30	2.19
512	2.33	2.31	2.14
1024	2.34	2.35	2.27
2048	2.38	2.30	2.28

Benzilic Acid

Table XLVI.—Molecular Conductivity

V	35°	50°	65°
128	114.3	...	...
512	192.4	220.6	240.4
1024	237.1	266.5	293.0
2048	281.4	320.8	348.5

Table XLVIII.—Temperature Coefficients

	35°–50°		50°–65°	
V	Cond. units	Per cent.	Cond. units	Per cent.
128	....	....	....	....
512	1.88	0.98	1.29	0.58
1024	1.96	0.83	1.77	0.66
2048	2.63	0.93	1.85	0.58

Table XLIX.—Percentage Dissociation

V	35°	50°	65°
128	29.97	...	...
512	47.57	48.01	46.24
1024	60.20	58.11	56.36
2048	64.82	69.95	67.03

Table L.—Dissociation Constants $\times 10^4$

V	35°	50°	65°
128	9.46	....	....
512	8.43	8.66	7.77
1024	8.89	7.87	7.09
2048	5.83	7.95	6.65

Meconic Acid

Table LI.—Molecular Conductivity

V	35°	50°	65°
32	461.5	524.4	574.2
128	599.0	684.7	754.9
512	728.9	839.2	940.8
1024	778.3	899.0	1027.8
2048	803.2	945.0	1081.2

Table LII.—Temperature Coefficients

	35°–50°		50°–65°	
V	Cond. units	Per cent.	Cond. units	Per cent.
32	4.19	0.91	3.32	0.63
128	5.72	0.94	4.68	0.68
512	7.31	1.00	6.77	0.80
1024	8.07	1.04	8.59	0.96
2048	9.49	1.18	9.08	0.96

o-*Chlorobenzoic Acid*

Table LIII.—Molecular Conductivity

V	35°	50°	65°
128	128.6	138.4	143.1
256	168.7	182.3	189.3
512	211.8	231.8	240.1
1024	256.3	281.9	298.8
2048	294.7	329.2	350.5

Table LIV.—Temperature Coefficients

	35°–50°		50°–65°	
V	Cond. units	Per cent.	Cond. units	Per cent.
128	0.67	0.52	0.313	0.23
256	1.01	0.60	0.467	0.26
512	1.33	0.63	0.553	0.24
1024	1.70	0.66	1.13	0.40
2048	2.15	0.73	1.42	0.43

Table LV.—Percentage Dissociation

V	35°	50°	65°
128	32.32	29.56	28.70
256	42.06	38.95	37.97
512	53.33	49.53	48.16
1024	64.53	60.23	49.94
2048	74.74	70.34	70.31

Table LVI.—Dissociation Constants $\times 10^4$

V	35°	50°	65°
128	12.1	0.97	0.90
256	11.9	0.97	0.91
512	11.9	0.95	0.87
1024	11.5	0.89	0.88
2048	10.8	0.82	0.82

o-*Nitrobenzoic Acid*[1]

Table LVII.—Molecular Conductivity

V	35°	50°	65°
32	138.0	144.9	147.2
128	223.6	240.8	249.9
512	308.7	345.9	370.6
1024	347.8	393.5	426.8
2048	369.8	425.9	474.4

[1] Measurements made by Dr. H. R. Kreider.

Table LVIII.—Temperature Coefficients

	35°–50°		50°–65°	
V	Cond. units	Per cent.	Cond. units	Per cent.
32	0.29	0.20	0.15	0.11
128	1.21	0.54	0.61	0.25
512	2.54	0.83	1.65	0.48
1024	3.77	1.12	2.22	0.55
2048	4.94	1.40	3.23	0.75

Table LIX.—Percentage Dissociation

V	35°	50°	65°
32	35.2	30.91	27.53
128	55.7	51.36	46.74
512	77.0	73.78	69.31
1024	84.2	83.94	79.82
2048	88.0	90.86	88.72

Table LX.—Dissociation Constants × 10^4

V	35°	50°	65°
32	59.7	43.2	32.7
128	54.7	42.4	32.1
512	50.3	32.2	30.6
1024	43.7	42.8	30.8
2048	34.4	55.2	34.1

m-*Nitrobenzoic Acid*[1]

Table LXI.—Molecular Conductivity

V	35°	50°	65°
128	77.56	89.9	99.9
512	137.1	160.1	177.9
1024	175.4	210.7	235.9
2048	216.7	262.9	295.7

Table LXII.—Temperature Coefficients

	35°–50°		50°–65°	
V	Cond. units	Per cent.	Cond. units	Per cent.
128	0.82	1.06	0.67	0.74
512	1.53	1.12	1.19	0.74
1024	2.35	1.34	1.67	0.78
2048	3.08	1.42	2.19	0.83

[1] Measurements made by Dr. H. R. Kreider.

Table LXIII.—Percentage Dissociation

v	35°	50°	65°
128	19.2	19.1	18.7
512	33.9	34.1	33.2
1024	43.4	44.9	44.0
2048	53.6	56.0	55.2

Table LXIV.—Dissociation Constants × 10⁴

v	35°	50°	65°
128	3.57	3.54	3.34
512	3.40	3.44	3.32
1024	3.25	3.57	3.38
2048	3.02	3.48	3.33

p-*Nitrobenzoic Acid*

Table LXV.—Molecular Conductivity

v	35°	50°	65°
512	147.7	170.6	187.9
1024	189.9	218.7	238.6
2048	235.0	275.2	304.2

Table LXVI.—Temperature Coefficients

	35°–50°		50°–65°	
v	Cond. units	Per cent.	Cond. units	Per cent.
512	1.49	1.00	1.15	0.67
1024	2.09	1.12	1.33	0.61
2048	2.65	1.13	1.93	0.70

Table LXVII.—Percentage Dissociation

v	35°	50°	65°
512	37.12	36.45	35.18
1024	46.86	46.73	44.76
2048	58.87	58.80	57.07

Table LXVIII.—Dissociation Constants × 10⁴

v	35°	50°	65°
512	4.28	4.08	3.52
1024	4.03	4.00	3.54
2048	4.11	4.09	3.70

1,2,4-Dinitrobenzoic Acid

Table LXIX.—Molecular Conductivity

V	35°	50°	65°
32	259.4	284.5	301.6
128	333.8	376.2	412.0
512	381.2	443.4	493.2
1024	391.5	459.8	512.6
2048	398.1	466.7	525.4

Table LXX.—Temperature Coefficients

	35°–50°		50°–65°	
V	Cond. units	Per cent.	Cond. units	Per cent.
32	1.53	0.63	1.14	0.40
128	2.66	0.79	2.39	0.64
512	4.30	1.14	3.32	0.75
1024	4.59	1.17	3.52	0.77
2048	4.66	1.17	3.91	0.84

Table LXXI.—Percentage Dissociation

V	35°	50°	65°
32	65.49	61.04	57.40
28	84.74	80.71	78.42
512	95.47	95.13	93.87
1024	98.49	98.65	97.56
2048	100.00	100.00	100.00

1,3,5-Dinitrobenzoic Acid

Table LXXII.—Molecular Conductivity

V	35°	50°	65°
512	335.6	279.7	311.8
1024	280.9	328.7	366.0
2048	324.5	382.1	426.9

Table LXXIII.—Temperature Coefficients

	35°–50°		50°–65°	
V	Cond. units	Per cent.	Cond. units	Per cent.
512	3.08	1.32	2.14	0.77
1024	3.25	1.16	2.49	0.76
2048	3.84	1.19	3.16	0.74

Table LXXIV.—Percentage Dissociation

V	35°	50°	65°
512	58.83	59.93	59.35
1024	70.54	70.43	69.66
2048	78.86	81.31	81.25

Table LXXV.—Dissociation Constants × 10^4

V	35°	50°	65°
512	16.4	17.5	16.4
1024	16.5	16.4	15.6
2048	14.4	17.3	17.2

m-*Hydroxybenzoic Acid*[1]

Table LXXVI.—Molecular Conductivity

V	35°	50°	65°
64	27.74	31.74	34.75
128	38.63	44.46	48.77
512	73.28	83.92	92.10
1024	99.70	116.0	127.5
2048	132.6	151.9	167.6

Table LXXVII.—Temperature Coefficients

	35°–50°		50°–65°	
V	Cond. units	Per cent.	Cond. units	Per cent.
64	0.27	0.98	0.20	0.64
182	0.39	1.01	0.29	0.64
512	0.71	0.97	0.54	0.64
1024	1.09	1.09	0.77	0.66
2048	1.29	0.99	1.04	0.68

Table LXXVIII.—Percentage Dissociation

V	35°	50°	65°
64	6.88	6.7	6.4
128	9.58	9.4	9.1
512	18.19	17.7	17.1
1024	24.74	24.5	23.6
2048	32.91	32.1	31.1

Table LXXIX.—Dissociation Constants × 10^4

V	35°	50°	65°
64	0.795	0.755	0.694
128	0.794	0.764	0.689
512	0.798	0.745	0.687
1024	0.794	0.752	0.692
2048	0.788	0.743	0.685

Measurements made by Dr. H. R. Kreider.

p-*Hydroxybenzoic Acid*[1]

Table LXXX.—Molecular Conductivity

V	35°	50°	65°
65	16.94	19.41	21.43
128	23.38	26.70	29.38
512	45.33	51.95	57.15
1024	63.66	72.92	80.22
2048	86.67	99.51	109.38

Table LXXXI.—Temperature Coefficients

	35°–50°		50°–65°	
V	Cond. units	Per cent.	Cond. units	Per cent.
64	0.16	0.94	0.13	0.69
128	0.20	0.84	0.27	0.67
512	0.41	0.90	0.35	0.68
1024	0.65	1.00	0.49	0.67
2048	0.93	1.01	0.66	0.67

Table LXXXII.—Percentage Dissociation

V	35°	50°	65°
64	4.21	4.11	3.98
128	5.88	5.65	5.46
512	11.36	11.00	10.62
1024	15.70	15.43	14.91
2048	21.00	21.07	20.33

Table LXXXIII.—Dissociation Constants $\times 10^4$

V	35°	50°	65°
64	0.289	0.275	0.258
128	0.287	0.267	0.246
512	0.284	0.239	0.245
1024	0.285	0.275	0.261
2048	0.273	0.275	0.253

1,2,4-Dihydroxybenzoic Acid

Table LXXXIV.—Molecular Conductivity

V	35°	50°	65°
128	92.25	109.2	122.2
512	160.3	189.7	211.9
1024	205.6	241.4	266.7
2048	253.6	294.4	322.1

Measurements made by Dr. H. R. Kreider.

Table LXXXV.—Temperature Coefficients

	35°–50°		50°–65°	
V	Cond. units	Per cent.	Cond. units	Per cent.
128	1.14	1.24	0.863	0.79
512	1.85	1.14	1.48	0.78
1024	2.52	1.24	1.69	0.70
2048	3.08	1.24	1.85	0.63

Table LXXXVI.—Percentage Dissociation

V	35°	50°	65°
128	23.10	23.35	22.94
512	40.62	40.48	39.78
1024	51.04	51.63	50.07
2048	62.24	62.96	60.48

Table LXXXVII.—Dissociation Constants × 10^4

V	35°	50°	65°
128	5.42	5.06	5.33
512	5.43	5.38	5.13
1024	5.12	5.38	4.90
2048	5.01	5.23	4.52

m-*Aminobenzoic Acid*[1]

Table LXXXVIII.—Molecular Conductivity

V	0°	18°	25°	35°
128	3.57	6.91	8.54	11.09
512	6.16	10.33	12.17	14.96
1024	11.75	22.61	27.77	35.57
2048	17.20	32.38	39.37	50.01

Table LXXXIX.—Temperature Coefficients

	0°–18°		18°–25°		25°–35°	
V	Cond. units	Per cent.	Cond. units	Per cent.	Cond. units	Per cent.
128	0.19	5.3	0.23	3.3	0.25	2.9
512	0.23	3.7	0.25	2.4	0.28	2.3
1024	0.60	5.3	0.74	3.3	0.78	2.5
2048	0.84	4.9	1.00	3.0	1.06	2.7

Table XC.—Percentage Dissociation

V	0°	18°	25°	35°
128	1.69	2.26	2.57	2.82
512	2.97	3.38	3.66	3.80
1024	5.57	7.39	8.35	9.04
2048	8.15	10.59	11.83	12.71

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[1] The Ostwald dilution law would not give dissociation constants for this acid.

p-*Sulphamidobenzoic Acid*

Table XCI.—Molecular Conductivity

V	35°	50°	65°
512	127.9	148.3	163.5
1024	167.3	189.1	213.1
2048	209.6	243.9	270.5

Table XCII.—Temperature Coefficients

	35°–50°		50°–65°	
V	Cond. units	Per cent.	Cond. units	Per cent.
512	1.35	1.06	1.01	0.68
1024	1.45	0.87	1.27	0.67
2048	2.26	1.08	1.77	0.75

Table XCII.—Percentage Dissociation

V	35°	50°	65°
512	32.17	31.67	30.64
1024	42.01	40.38	39.93
2048	52.79	52.08	50.69

Table XCIII.—Dissociation Constants $\times 10^4$

V	35°	50°	65°
512	2.98	2.87	2.64
1024	2.97	2.67	2.59
2048	2.88	2.76	2.54

Benzenesulphonic Acid

Table XCIV.—Molecular Conductivity

V	35°	50°	65°
8	366.1	429.3	484.9
32	370.1	453.0	515.4
128	399.8	473.9	540.6
512	407.0	475.3	544.3
1024	410.3	474.2	544.2
2048	407.1	472.9	540.1

Table XCV.—Temperature Coefficients

	35°–50°		50°–65°	
V	Cond. units	Per cent.	Cond. units	Per cent.
8	4.21	1.15	3.71	0.86
32	5.53	1.49	4.16	0.92
128	4.94	1.23	4.45	0.94
512	4.55	1.12	4.60	0.97
1024	4.26	1.04	4.67	0.98
2048	4.39	1.08	4.48	0.95

Table XCVI.—Percentage Dissociation

V	35°	50°	65°
8	89.23	90.32	89.09
32	90.20	95.30	94.69
128	97.44	99.70	99.30
512	99.20	100.00	100.00
1024	100.00	100.00	100.00

m-*Nitrobenzenesulphonic Acid*

Table XCVII.—Molecular Conductivity

V	35°	50°	65°
32	347.2	409.0	465.5
128	357.3	419.5	478.4
512	366.8	430.4[1]	489.5
1024	367.9	432.6	491.0
2048	366.5	...	...

Table XCVIII.—Temperature Coefficients

	35°–50°		50°–65°	
V	Cond. units	Per cent.	Cond. units	Per cent.
32	3.93	1.12	3.77	0.92
128	4.15	1.16	3.93	0.94
512	4.24	1.15	3.94	0.92
1024	4.21	1.14	3.89	0.90

Table XCIX.—Percentage Dissociation

V	35°	50°	65°
32	94.75	94.54	94.80
128	96.69	96.97	97.43
512	99.40	99.49	99.69
1024	100.00	100.00	100.00

p-*Toluenesulphonic Acid*

Table C.—Molecular Conductivity

V	35°	50°	65
32	363.2	430.3	489.4
128	374.7	440.0	499.3
512	376.8	444.2	502.0
1024	380.3	445.9	503.4
2048	379.8	445.3	502.6

[1] Interpolated value.

Table CI.—Temperature Coefficients

	35°–50°		50°–65°	
V	Cond. units	Per cent.	Cond. units	Per cent.
32	4.59	1.27	3.94	0.92
128	4.39	1.17	3.95	0.90
512	4.52	1.20	3.85	0.87
1024	4.44	1.17	3.83	0.86
2048	4.89	1.31	3.82	0.86

Table CII.—Percentage Dissociation

V	35°	50°	65°
32	95.30	96.50	97.20
128	98.68	98.67	99.19
512	99.26	99.61	99.72
1024	100.00	100.00	100.00

1,4,2-Nitrotoluenesulphonic Acid

Table CIII.—Molecular Conductivity

V	0°	16°	25°
8	203.0	281.8	320.5
32	221.6	308.7	349.5
128	225.3	312.8	355.6
512	228.3	317.5	360.7
1024	228.9	318.5	362.3
2048	228.0	318.7	360.8

Table CIV.—Temperature Coefficients

	0°–16°		16°–25°		25°–35°	
V	Cond. units	Per cent.	Cond. units	Per cent.	Cond. units	Per cent.
8	4.90	2.41	4.30	1.53	4.38	1.37
32	5.42	2.44	4.53	1.47	4.36	1.25
128	5.44	2.41	4.76	1.52	5.20	1.46
512	5.55	2.43	4.80	1.51	5.11	1.42
1024	5.58	2.44	4.87	1.53	4.95	1.37
2048	5.65	2.48	4.68	1.47	5.14	1.42

Table CV.—Percentage Dissociation

V	0°	16°	25°
8	88.68	88.48	88.46
32	96.81	96.92	96.47
128	98.43	98.21	98.15
512	99.74	99.69	99.56
1024	100.00	100.00	100.00

1,4,2-Nitrotoluenesulphonic Acid

Table CVI.—Molecular Conductivity

V	35°	50°	65°
8	364.3	433.3	493.4
32	393.1	462.1[1]	524.8
128	407.6	476.7	542.6
512	411.8	486.0	554.5
1024	413.6	487.5	556.3
2048	412.2	485.4	553.2

Table CVII.—Temperature Coefficients

	35°–50°		50°–65°	
V	Cond. units	Per cent.	Cond. units	Per cent.
8	4.60	1.26	4.01	0.92
32	4.60	1.17	4.18	0.91
128	4.61	1.13	4.39	0.92
512	4.95	1.20	4.57	0.94
1024	4.92	1.19	4.59	0.94
2048	4.88	1.18	4.52	0.93

Table CVIII.—Percentage Dissociation

V	35°	50°	65°
8	88.08	88.88	88.69
32	95.04	94.79	94.34
128	98.55	97.78	97.54
512	99.56	99.69	99.67
1024	100.00	100.00	100.00

Dichlorophthalic Acid

Table CIX.—Molecular Conductivity

V	35°	50°	65°
128	318.9	354.7	378.7
512	397.5	451.7	492.5
1024	441.6	499.3	543.3
2048	493.0	562.8	614.0

Table CX.—Temperature Coefficients

	35°–50°		50°–65°	
V	Cond. units	Per cent.	Cond. units	Per cent.
128	2.42	0.76	1.60	0.45
512	3.55	0.89	2.72	0.60
1024	3.91	0.89	2.93	0.59
2048	5.02	1.03	3.41	0.60

Interpolated value.

Tetrachlorophthalic Acid

Table CXI.—Molecular Conductivity

V	35°	50°	65°
512	492.6	552.7	601.3
1024	555.2	617.4	669.3
2048	605.5	684.9	739.6

Table CXII.—Temperature Coefficients

	35°–50°		50°–65°	
V	Cond. units	Per cent.	Cond. units	Per cent.
512	4.00	0.81	3.24	0.59
1024	4.15	0.75	3.46	0.56
2048	5.33	0.88	3.65	0.53

Camphoric Acid

Table CXIII.—Molecular Conductivity

V	35°	50°	65°
512	42.27	47.53	51.30
1024	57.54	63.86	69.26
2048	76.74	86.20	93.84

Table CXIV.—Temperature Coefficients

	35°–50°		50°–65°	
V	Cond. units	Per cent.	Cond. units.	Per cent.
512	0.33	0.78	0.258	0.54
1024	0.39	0.67	0.360	0.56
2048	0.69	0.91	0.509	0.59

Table CXV.—Percentage Dissociation

V	35°	50°	65°
512	10.85	10.37	9.88
1024	14.78	13.94	13.34
2048	19.40	18.81	18.08

Table CXVI.—Dissociation Constants $\times 10^4$

V	35°	50°	65°
512	0.259	0.234	0.212
1024	0.250	0.220	0.201
2048	0.228	0.213	0.195

Discussion

It can be readily seen from the figures given above for the temperature coefficients that the statement in the introduction concerning them at lower temperature holds good up to 65°. It should be noted, however, that the temperature coefficients in per cent. have become at 65°—except with the strong acids—almost negligible.

The statement was made previously that these coefficients usually decrease with increase in dilution. A more careful study shows that no such general statement can be made. A large number increase, and some are quite irregular. The increase in the case of *o*- and *m*-nitrobenzoic acids, and one or two others, is especially worthy of mention. The variation amounts to fifty per cent. or more between the most concentrated and the most dilute solutions.

Whatever the reasons for the irregularity in connection with the temperature coefficients expressed in per cent., the fact that there is no general uniformity indicates a complicated state of affairs. We usually speak of conductivity being determined by the number and velocity of the ions—the number depending upon the amount of dissociation, which, in turn, is a function of the association of the solvent, the concentration, and the temperature, and perhaps of other causes of which we are not yet fully aware; the velocity being a function of the viscosity of the solution, the ionic volume and the specific character of the ion. Owing to the close interrelationship of these various factors, which may all be varying at once, it is almost impossible to predict the result of combining them.

The work at higher temperatures shows that the statement made in the previous work concerning the change in dissociation of the organic acids with change in temperature is correct, so far as it goes. A more general statement, however, can now be made. Whatever the change in dissociation at lower temperatures—with some acids there is a constant decrease from 0°, with others a maximum value at some intermediate temperature—there is in every case a decrease in the dissociation in passing from fifty degrees to any higher temperature.

Mention has already been made of the fact that the μ_∞ values for the dibasic acids are not as readily obtained at 50° and 65° as at the lower temperatures, on account of fewer of the values for μ_∞ falling on a definite curve when plotted against the number of atoms in the anion.

Since the μ_∞ values for several of the strong acids, and some others, even at lower temperatures, do not fit into this curve, it is safe to say that there is some other factor in addition to the mere number of atoms in the anion which likewise affects the magnitude of the μ_∞ value. Perhaps their arrangement has some influence, but more likely the amount of hydration which, of course, changes the size and mass of the anion, and which has not been taken into account in this work, plays a very important part.

Rise in temperature does not produce exactly the same effect on every hydrated substance, and we would expect a greater variation in the effect produced at higher than at lower temperatures. It might be claimed that the acids are not sufficiently hydrated to be thus affected. Not so with the sodium salts of the acids, however, and it is by means of them that the μ_∞ values are obtained for the monobasic acids.

All other conclusions reached heretofore have been confirmed in the present work, and as they have already been summarized in the introduction to the present paper further mention of them is not necessary.

SUMMARY

No conclusion, in explanation of the irregularities in the percentage temperature coefficients, could be arrived at, except that they are the result of a large number of varying factors which are closely interrelated.

Higher temperature causes a decrease in dissociation.

The values of μ_∞ for the organic acids, plotted against the number of atoms in the anion, do not give a very even curve. The cause for this probably lies in the fact that the sodium salts, from the μ_∞ values of which the μ_∞ values of the acids are obtained, are more or less hydrated and the rising temperature produces varying effects

Work is now in progress on a much larger number of organic acids, and these substances will also be studied in nonaqueous and mixed solvents.

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BALTIMORE, MD.
May, 1912

ON THE MECHANISM OF ORGANIC REACTIONS

BY S. F. ACREE

[TWELFTH COMMUNICATION ON CATALYSIS]

(We have been aided in these researches by the Carnegie Institution of Washington.)

ALKALINE CATALYSIS

As a further contribution to our theory that in all reactions we should consider the possibility of the direct transformation of both ions and nonionized[1] substances the writer presents[2] work by Dr. H. C. Robertson, Dr. E. K. Marshall, Dr. Julia Peachy Harrison, Miss B. Marion Brown, Dr. J. Chandler, Dr. Sidney Nirdlinger, Dr. F. M. Rogers, Dr. C. N. Myers and Mr. J. H. Shrader on the reactions of alkyl halides with sodium, potassium and lithium ethylates, with sodium, potassium and lithium phenolates, and with sodium phenylthiourazole, and on the reversible addition of ethyl alcohol to nitriles when catalyzed by ethylates, in absolute ethyl alcohol. We are showing, furthermore, how the theory is aided by the work of Stieglitz, of Goldschmidt and of Tubandt. The experimental and mathematical details of our researches will appear soon as publications in THIS JOURNAL and as a monograph of the Carnegie Institution of Washington.

If the ethylate ion reacts with the molecular alkyl halide and forms the halide ion and an ether, and the nonionized sodium ethylate also reacts with the molecular alkyl halide and yields the sodium halide and the ether, the reaction can be represented as follows:

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[1] THIS JOURNAL, **27,** 118; **28,** 370; **31,** 185; **32,** 606; **37,** 71, 361; **38,** 1, 258, 489, 746; **39,** 124, 145, 226, 300; **41,** 457, 483; **42,** 115; **43,** 358, 505; **44,** 219. Ber. d. chem. Ges., **33,** 1520; **35,** 553; **36,** 3139; **37,** 184, 618; **41,** 3199. Science, **30,** 617 (1909). J. Am. Chem. Soc., **30,** 1755.

[2] A short article on this subject was presented at the New York meeting of the Int. Congress of Applied Chem., September, 1912.

$$C_2H_5I + \overset{-}{O}C_2H_5 \longrightarrow (C_2H_5)_2O + \overset{-}{I}$$

$$C_2H_5I + \left\{\begin{matrix} NaOC_2H_5 \text{ or} \\ \overset{+}{Na} + \overset{-}{O}C_2H_5 \end{matrix}\right\} \longrightarrow (C_2H_5)_2O + NaI, \text{ or}$$

$$\begin{aligned} \frac{dx}{dt} &= K_i\alpha(C_{salt} - x)(C_{alkyl\ halide} - x) \\ &\quad + K_m(1 - \alpha)(C_{salt} - x)(C_{alkyl\ halide} - x) \\ &= [K_i\alpha + K_m(1 - \alpha)](C_{salt} - x)(C_{alkyl\ halide} - x) \\ &= K_V(C_{salt} - x)(C_{alkyl\ halide} - x) \end{aligned}$$

K_i (see note, p. 378) is the reaction velocity of the alkyl halide and the ethylate (phenolate, urazole, etc.) anion, K_m is the reaction velocity of the alkyl halide and the nonionized sodium ethylate (potassium ethylate, etc.), α is the per cent. of ionization of the sodium ethylate as determined by the conductivity method by Dr. H. C. Robertson, C_{salt} is the initial concentration of the sodium ethylate, i. e., one gram molecule in V liters, $C_{alkyl\ halide}$ is the initial concentration of the alkyl halide, and x is the change in the concentration of the sodium ethylate and of the alkyl halide in the time t.

On integration we get the equations

$$K_V = K_i\alpha + K_m(1 - \alpha) = \frac{x}{t(A - x)} \text{ or } \frac{B}{t(A - B)} \text{logn} \frac{B(A - x)}{A(B - x)}$$

When the values of K_V are multiplied by V we secure the expressions

$$\begin{aligned} VK_V &= K_n = K_i\alpha + K_m(1 - \alpha) \\ V'K_{V'} &= K'_n = K_i\alpha' + K_m(1 - \alpha') \\ V''K_{V''} &= K''_n = K_i\alpha'' + K_m(1 - \alpha'') \end{aligned}$$

which give us the reaction velocity, K_n, K'_n or K''_n, which the solution would have if the concentration of the sodium ethylate were unity and the ionization were α, α' or α''. When these equations are solved simultaneously we secure the unknown values of K_i and K_m from the expressions

$$K_i = \frac{K'_n(1-\alpha)-K_n(1-\alpha')}{\alpha'-\alpha}$$

and

$$K_m = \frac{K_n\alpha' - K'_n\alpha}{\alpha'-\alpha}.$$

The various values of K_i and K_m so obtained should be, and are, constant within the experimental errors, whatever the value of V. Since we have measured the ionization and reaction velocities of the ethylates in solutions varying from N/1 to N/32 there is a wide variation in K_V and α; but the values of K_i and K_m for sodium ethylate and methyl iodide are found by Dr. Robertson to be quite constant and to give the average $K_i = 0.127$ and $K_m = 0.0594$ (see Table III below). These results make plausible our interpretation that both the ethylate ions and the nonionized sodium ethylate react with the alkyl halides.

In the following tables are given as briefly as possible, as an example, some of the experimental results which Dr. H. C. Robertson has obtained for a typical case, the reaction of sodium ethylate with methyl iodide at 25°. In Table I are given the values of α and $(1-\alpha)$ corresponding to the different values of V. Each value of K_n in Table II is the mean of a large number obtained when the reactions were allowed to take place during different intervals of time. The values of K_i and K_m with asterisks in Table III are those in which there are smaller experimental errors involved in $\alpha'-\alpha$ and other factors. As is generally the case, the average of these values with least errors is practically the same as the average of all the values obtained. In Table IV we give a comparison of K_n "found" and K_n "calculated" from the values of K_i and K_m; the magnitude of the experimental errors is thus clearly shown. Naturally all of these results are subject to the slight revision which must always accompany a more careful repetition of any investigation.

Table I.—Ionization of Sodium Ethylate at 25°

V	α	$(1-\alpha)$
1	0.148	0.852
2	0.234	0.766
4	0.312	0.688
8	0.393	0.607
16	0.481	0.519
40	0.605	0.395

Table II.—Values of K_n for Sodium Ethylate and Methyl Iodide at 25°

V	K_n	K_n (average)
2	0.0748	0.0750
	0.0752	
4	0.0812	0.0808
	0.0804	
8	0.0856	0.0857
	0.0858	
16	0.0923	0.0923
	0.0923	
40	0.1020	0.0998
	0.0976	

Table III.—K_i and K_m for Sodium Ethylate and Methyl Iodide at 25°

V	K_i	K_m
$V=2$: $V=4$	0.132	0.0577
$V=2$: $V=8$	0.127*	0.0591*
$V=2$: $V=16$	0.129*	0.0586*
$V=2$: $V=40$	0.126*	0.0593*
$V=4$: $V=8$	0.123	0.0616
$V=4$: $V=16$	0.127*	0.0595*
$V=4$: $V=40$	0.125*	0.0605*
$V=8$: $V=16$	0.130	0.0567
$V=8$: $V=40$	0.126*	0.0597*
$V=16$: $V=40$	*0.124*	*0.0632*
Average	0.127	0.0596
Average[1]	0.127	0.0594

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[1] The average of all values with asterisks involves smaller errors.

Table IV.—K_n "Found" and K_n "Calculated" for Sodium Ethylate and Methyl Iodide at 25°

		K_n calculated		Error in per cent.	
V	K_n found	(1) $\begin{cases} K_i = 0.1270 \\ K_m = 0.0596 \end{cases}$	(2) $\begin{cases} K_i = 0.1270 \\ K_m = 0.0594 \end{cases}$	(1)	(2)
2	0.0750	0.0753	0.0752	—0.4	—0.3
4	0.0808	0.0807	0.0805	+0.1	+0.4
8	0.0857	0.0861	0.0860	—0.5	—0.4
16	0.0923	0.0920	0.0919	+0.3	+0.5
40	0.0998	0.1004	0.1002	—0.6	—0.4

But if this theory is correct we should obtain the same value for K_i *for the ethylate ion* when we study the reaction of methyl iodide with sodium ethylate and with potassium ethylate, although the values of K_m may differ in the two reactions. Still more conclusive evidence for the theory, therefore, is the fact that Dr. Julia P. Harrison finds that potassium ethylate and methyl iodide, in solutions varying from 0.25 N to 0.03125 N, give the same average value, $K_i = 0.127$, for the ethylate ion that Dr. Robertson obtains from sodium ethylate and methyl iodide. This is especially striking in view of the fact that the molecular potassium ethylate, for which $K_m = 0.066$ for this reaction, reacts 12 per cent. faster with the methyl iodide than does the molecular sodium ethylate.

Another line of evidence for our theory is the fact that in *dilute solutions* the addition of sodium iodide to sodium ethylate and methyl iodide, for example, suppresses the ionization of the sodium ethylate, and therefore its reaction velocity, to exactly the extent that we calculate from the Arrhenius theory of isohydric solutions and from our theory of the mechanism of this class of reactions. When several equivalents of sodium iodide are added to one of sodium ethylate (N/32) the reaction velocity is slightly smaller than the theoretical value. Dr. H. C. Robertson has shown experimentally that the Arrhenius theory of isohydric solutions applies closely in all of our work. When an added salt changes the reaction velocity exactly as demanded by our theory we consider the "salt effect" to be "normal." When the concentration of the added salt becomes so large that the reaction velocity does not correspond exactly to the calculated value, we call this deviation a positive or negative[1] "abnormal salt effect." We believe that an "abnormal salt effect" is due to a change in the physical conditions of the solution, or to the formation of *new double compounds* which are more or less reactive than the constituent parts, either of which causes will be most evident in the concentrated solutions. We are studying the question whether the ionic and molecular reactions are affected alike by the ions and nonionized salts.

Still other satisfactory evidence for the theory is the fact that Dr. H. C. Robertson and Mr. J. H. Shrader have shown that sodium phenolate, potassium phenolate and lithium phenolate have different degrees of ionization in the same concentrations and react with different velocities with methyl iodide, and yet these three salts, in concentrations varying from N to 0.03125 N, give the same value for K_i, namely 0.0282, 0.0283 and 0.0284, respectively. The values of K_m are 0.00474, 0.0037 and 0.0040, respectively, this wide variation harmonizing very nicely with our theory because of the differences in the nonionized sodium, potassium and lithium phenolates. Added sodium iodide produces a positive "abnormal salt effect."

Dr. J. Chandler proved, as did also Dr. Sidney Nirdlinger and Dr. F. M. Rogers working together,[2] that ethyl iodide reacts with both the anion and the nonionized portion of the cyclic amide[3] sodium phenylthiourazole in ethyl alcohol at

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[1] For the equations covering such cases see Acree and coworkers: Ber. d. chem. Ges., **41**, 3208. e. g., $[1+(f)\ C_{salt}][K_i\alpha+K_m(1-\alpha)](C_{salt}-x)(C_{alkyl\ halide}-x)$.

[2] This work was finished in May, 1908, and reported in THIS JOURNAL, **43**, 519, 551. Although recognizing the possibility of the reaction of the nonionized salt, we interpreted the first crude data of Shadinger, Brunel and Johnson as reactions "chiefly" of the urazole anions (THIS JOURNAL, **39**, 228–236). In THIS JOURNAL, **38**, 261, we wrote: "If the other urazole groups are concerned in the reaction it is to only a minor extent." The final work now shows the nonionized salt to be more reactive than we then believed.

[3] It is possible that in the Hofmann and Lossen rearrangements both tautomeric forms of the amide salt react intramolecularly with the NBr group, for instance, just as the urazole salts do with an alkyl bromide. In this connection it was pointed out by the writer at the Boston meeting of the A. A. A. S., in 1909, that such changes as the Hofmann rearrangement of chloro- and bromoamides, the Lossen rearrangement of hydroxamic derivatives (see L. W. Jones: THIS JOURNAL, **48**, 1, for an excellent dis-

25°. The solutions were varied in concentration from N/3 to *N*/64. Dr. Chandler found the values $K_i = 0.465$ and $K_m = 0.16$. Dr. Nirdlinger and Dr. Rogers obtained the values $K_i = 0.43$ and $K_m = 0.17$ in their work; the solutions contained small quantities of water, which lowers the reaction velocity. The addition of sodium iodide suppressed the ionization and reaction velocity of the sodium phenylthiourazole practically exactly the amount calculated from our theory; the "salt effect" was "normal" even when three equivalents of sodium iodide were added to one of the sodium urazole (N/64).

We have also made calculations on the excellent data of Tubandt[1] involving the inversion of menthone by sodium ethylate in absolute ethyl alcohol, and have found that both the ethylate ions and the sodium ethylate molecules seem to invert the menthone with the same[2] velocity; that is, $K_i =$

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cussion), and also the Beckmann rearrangement of oximes by acids, may be due to a monomolecular rearrangement of the *ion* as well as of the *nonionized salt*.

$$\left\{\begin{array}{c}\mathrm{C_6H_5CONKBr}\\ \text{and}\\ \mathrm{C_6H_5C(OK):NBr}\end{array}\right\} \longrightarrow \mathrm{C_6H_5N:C:O + KBr}$$

$$\left\{\begin{array}{c}\mathrm{C_6H_5CO\overline{N}Br}\\ \text{and}\\ \mathrm{C_6H_5C(\overline{O}):NBr}\end{array}\right\} \longrightarrow \mathrm{C_6H_5N:C:O} + \overline{\mathrm{Br}}$$

$$\frac{dx}{dt} = K_i\alpha(C_{salt} - x) + K_m(1 - \alpha)(C_{salt} - x) = [K_i\alpha + K_m(1 - \alpha)](C_{salt} - x)$$

Van Dam (Rec. trav. chim., **18**, 408; **19**, 318) added varying amounts of alkalies to benzbromoamide and found that the reaction velocity increased with an increase in the concentration of the (alkali and) hydroxyl ions. He interpreted the change as *a pure catalysis* by the hydroxyl ions. The writer thinks it much more probable that the benzbromoamide was converted nearly completely into a salt according to the above equations, and that the addition of more alkali simply increased the concentration of the *nonionized salt* in accordance with the Arrhenius isohydric principle, and increased the reaction velocity because the nonionized salt decomposes faster than the ion. The relative magnitudes of K_i and K_m for all such cases should be accurately measured in water and in alcohol. Alcohol will probably be found more satisfactory as a solvent, as in our work, because of the greater changes in the ionization of the salt and the smaller errors involved in K_i and K_m. An article on this subject will soon be published by the writer. (NOTE.—Since this was written, Professor Stieglitz has informed the writer privately that his own experimental work has led him to conclusions similar to ours.)

[1] Ann. Chem. (Liebig), **339**, 41; **354**, 259; **377**, 284. The inversion of menthone by acids seems to involve the ions and molecules of the salt formed by the menthone and the acid.

[2] A similar case seems to be involved in Bredig's study (Z. Elektrochem., **10**, 582) of the change of benzaldehyde into benzoin by cyanides, which he interpreted as being due to a *pure catalysis* by the cyanide ions alone. Although the solvent was 66 per

K_m = 0.41 at 20° and 0.93 at 30°. The solutions containing sodium ethylate in concentrations varying from about 0.05 N to about 0.01 N are dilute enough to be practically ideal solutions, and are probably the ones having the smallest experimental errors; these give excellent data for our theory. The sodium ethylate acts *purely catalytically*, as it is not used up in the reaction. Especially important for the theory is the fact that Tubandt found that added sodium acetate, sodium dimethylhydroresorcinolate, sodium acetoacetic ester and sodium bromide, in various concentrations, have absolutely no "salt effect" on the reaction velocity. This absence of "salt effect" is to be predicted from our theory, and is "normal," whenever the nonionized sodium ethylate and the ethylate ions react with equal velocities; the change produced, by the added salt, in the relative number of ions and molecules of the ethylate can have no effect as long as the ethylate ion and the sodium ethylate molecules are equally active, and their total number remains constant, and no new active constituents are formed. It will be especially important to see whether the ethylate ion from sodium, potassium, lithium and thallium ethylates inverts the menthone with a constant velocity, or constant value for K_i. The values for K_m for the different ethylates may, and probably will, be found to be different, as we have found to be the case with the reactions of alkyl halides with different ethylates and phenolates.

Our theory of alkaline catalysis has been substantiated in still another way by work on imido esters. Stieglitz[1] and Schlesinger found that barium hydroxide decomposes imido esters into nitriles and alcohols, and they used the Ostwald-Arrhenius theory that the decomposition is due to the hydroxyl ions *alone*, as in the case of the saponification of ordinary esters by hydroxides. But we have recalculated their excel-

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cent. alcohol, and the concentration of the potassium cyanide varied from 0.05 N to 0.4 N. *Bredig assumed a constant per cent. of ionization of the salt in calculating* K_{cy} or K_i. *This assumption is extremely improbable.* Since there is only a very slight, if any, increase in K_n with increase in V, it is *very probable* that both the nonionized salt and the cyanide ions are active, the value K_i being only slightly, if at all, larger than K_m. It would be extremely interesting to see this problem studied in absolute ethyl alcohol from this point of view, by using a number of cyanides and aldehydes.

[1] This Journal, **39**, 738.

lent data and have found that the concentration of the barium hydroxide molecules is so small, about 3 to 7 per cent., *that their results can be interpreted fully as well on our theory that both the hydroxyl ions and the nonionized barium hydroxide are, in this case, equally active.* Our theory is completely substantiated in this connection by the work of Dr. E. K. Marshall and Dr. Julia Peachy Harrison, who have found sodium, potassium and lithium ethylates to catalyze the reversible[1] reaction of nitriles with ethyl alcohol,

$$CH_3CN + C_2H_5OH \rightleftarrows CH_3C(:NH)OC_2H_5$$

Just as sodium hydroxide decomposes an imido ester in water into a nitrile and an alcohol, so sodium ethylate, the analogue of sodium hydroxide, decomposes an imido ester in absolute ethyl alcohol *purely catalytically* into a nitrile and an alcohol. The advantage of studying this latter reaction is that the sodium ethylate is far less ionized in ethyl alcohol in the concentrations used than is the sodium hydroxide in aqueous solutions of the same concentrations. This enables us to measure more accurately any possible activity of the sodium ethylate molecules, and when this is done with solutions of sodium ethylate varying from 0.25 N to 0.015625 N we find indeed the values $K_i = 0.344$ and $K_m = 0.228$ for the decomposition of 0.25 N acetimido ethyl ester, and $K_i = 0.1148$ and $K_m = 0.1003$ for the change of 0.25 N benzimido ethyl ester. It should be especially emphasized, in this connection, that the addition of even several molecules of sodium iodide lowers the per cent. of ionization and the reaction velocity, or activity, of the sodium ethylate "normally," or to just the extent calculated from our theory. As was predicted, the "salt effect" of added sodium iodide is very small in this latter case, just as it is in the menthone work (see page 359) and in all cases in which the ethylate ions and the sodium ethylate molecules react with practically equal velocities.

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[1] Dr. E. K. Marshall has found this reaction to be reversible in every case studied by him, whether approached from the nitrile or from the imido ester. The equilibrium point varies from 1 per cent. nitrile to 98 per cent. nitrile when different nitriles, and the corresponding imido esters, are used. See Purdie: J. Chem. Soc., **39,** 344. Nef: Ann. Chem. (Liebig,) **287,** 280. Lengfeld and Stieglitz: THIS JOURNAL, **17,** 112. Stieglitz: Ber. d. chem. Ges., **28,** 573. McKee: THIS JOURNAL, **26,** 206; **36,** 209; **42,** 1. Dains: J. Am. Chem. Soc., **21,** 136.

Although this work on the action of ethylates on nitriles and imido esters in ethyl alcohol is presented only tentatively, *as we must work with several other ethylates to be certain that the reaction velocity of the ethylate ion is the same for all ethylates*, these experiments seem to show that both the ethylate ions and the sodium ethylate molecules, and perhaps also both the hydroxyl ions and the barium (sodium, etc.) hydroxide molecules, are concerned in the decomposition of imido esters into nitriles and alcohols.

It may be that both the hydroxyl ions and the nonionized bases react with esters in ordinary saponification.[1] Since the sodium hydroxide, for instance, is very largely ionized in the dilute aqueous solutions used, the activity of the nonionized base may be HIDDEN IN THE EXPERIMENTAL ERRORS on account of its small concentration and small activity. Miss B. Marion Brown is therefore attacking an analogous problem, the saponification of esters and thiol esters with sodium, potassium and lithium sulphydrates in absolute ethyl alcohol, to learn whether *both* the sulphydrate anion and the nonionized metallic sulphydrates react with the esters. The concentration of the nonionized sulphydrate is much larger in concentrated alcoholic solutions than in the corresponding aqueous solutions, and this fact will allow us to measure far more easily the activity of the nonionized sulphydrate towards the esters and secure possibly a deeper insight into the mechanism of the saponification of esters by alkalies.

We are planning the study of the analogous interchange[2] of alkyls when esters are treated with metallic alcoholates in the corresponding absolute alcohol.

$$\mathrm{RCOOCH_3 + NaOC_2H_5 + C_2H_5OH \text{ in excess} \longrightarrow}$$
$$\mathrm{RCOOC_2H_5 + NaOCH_3 + C_2H_5OH \text{ in excess} \longrightarrow}$$
$$\mathrm{RCOOC_2H_5 + NaOC_2H_5 + CH_3OH}$$

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[1] Acree and Johnson: THIS JOURNAL, **38**, 344; **39**, 524. This seems clearly to be the case in some recent studies by Holmberg (Z. physik. Chem., **79**, 147) and Johansson (*Ibid.*, **79**, 621) on the removal of halogens from the salts of halogenated acids by the action of alkalies.

[2] Claisen: Ber. d. chem. Ges., **20**, 646. Kremann: Monats. Chem., **26**, 783; **29**, 23. Henriques: Z. angew. Chem., **1898**, 338, 697. Goldschmiedt: Z. Elektrochem , **10**, 221. Kossel, Krüger, and Obermüller: Z. physiol. Chem., **15**, 321; **16**, 153.

The polariscope should be especially useful in studying these changes when the esters are optically active.

These results obtained by the various investigators in the study of the changes of nitriles and of menthone by ethylate are very important for our theory because the sodium ethylate acts as a *pure catalyst* in the older sense in that it is not measurably changed in concentration during the reaction. Notwithstanding this the mechanism of these reactions is essentially the same as that involving the ethylates and the alkyl halides, or the phenolates and the alkyl halides, in which the ethylate and the phenolate are decomposed completely into a sodium halide and an ether. Our theory enables us to predict that there is no essential difference between the cases of old style or pure catalysis, in which the catalyzer is not appreciably used up, and those cases in which the catalyzer is partially or completely changed into the end products.[1] All of the available trustworthy experimental evidence supports this point of view, as the following reasoning will show.

In the reaction of the sodium ethylate or sodium phenolate or sodium thiourazole with the alkyl halides *all of the ethylate or phenolate or urazole salt formed is decomposed with a velocity which is a function of the concentrations of the anions and of the molecules.* In the case of the menthone inversion and the alcohol-nitrile reaction the sodium ethylate does not apparently enter into the reaction and yet its activity is a function of the concentrations of the ethylate anions and of the sodium ethylate molecules. It is very likely, however, that the menthone and the nitrile, or the imido ester in the reverse reaction, actually do react with small amounts of the ethylate ions or sodium ethylate molecules and form salts and ions on account of the unsaturated carbonyl and nitrile groups and the acid character of the imido ester. This is illustrated in the case of the menthone inversion, for instance, by the following brief scheme, in which many possible intermediate reactions are omitted:

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[1] For a fuller discussion see Acree and Johnson: THIS JOURNAL, **38**, 258; **39**, 513. Ber. d. chem. Ges., **41**, 3199.

$$\underset{d\text{-menthone}}{C_9H_{18}CO} + \bar{O}C_2H_5 \rightleftarrows \underset{\text{(I)}}{C_9H_{18}C(\bar{O})OC_2H_5} \rightleftarrows \underset{l\text{-menthone}}{C_9H_{18}CO} + \bar{O}C_2H_5$$

$$\underset{d\text{-menthone}}{C_9H_{18}CO} + NaOC_2H_5 \rightleftarrows \underset{\text{(M)}}{C_9H_{18}C(ONa)OC_2H_5} \rightleftarrows$$

$$\underset{l\text{-menthone}}{C_9H_{18}CO} + NaOC_2H_5$$

If now only traces of (I) and (M) are formed, the concentrations of (I) and (M) are practically proportional to the products of the concentrations of the menthone and the ethylate ions, and of the menthone and the nonionized sodium ethylate, respectively. The real velocity of the reaction is strictly proportional to the concentrations of the ion (I) and of the nonionized salt (M), and we can repeat the above italicized words and say that *all of the ethylate-menthone compound formed is decomposed with a velocity which is a function of the concentration of the anions (I) and of the molecules (M).* Since we can insert in any equations the product *ethylate ion* × *menthone* instead of (I) and the product *sodium ethylate* × *menthone* instead of (*M*), and since, furthermore, the ethylate ions and sodium ethylate are constantly regenerated and remain in practically constant concentration, it is evident that the reaction velocities in these cases of *pure catalysis* are *apparently* and *indirectly* functions of the concentrations of the ethylate ions and the nonionized sodium ethylate, while *really* and *directly* functions of the concentrations of the ion (I) and the molecule (M), which are decomposed just as the ethylates and the phenolates are decomposed by the alkyl halides. This makes it clear that all cases of catalysis may be treated alike mathematically, the only differences being in the magnitude of the concentrations of (I) and (M), which can range from a small fraction of one per cent. to practically 100 per cent. of the theoretical. The mathematical side of this question has been treated fully in previous articles and is touched briefly again on pages 372–377.

ACID CATALYSIS

The sodium thiourazole and the sodium, potassium and lithium phenolates are formed by the addition of either the hydroxides or the ethylate of the alkali metal to the corresponding acid; when these salts react with alkyl halides we call these changes *cases of alkaline*[1] *catalysis* in order to compare them with *cases of catalysis by acids.* In the preceding paragraphs it was shown that *in alkaline catalysis we must consider the possibility of reactions of both the anions and the molecules of the reacting salt.*

The writer and Brunel[2] worked on the above ideas of alkaline catalysis and also on the problem that in the catalysis of esters by acids, *we must have traces of intermediate oxonium salts formed, the cations and the molecules of which may be hydrolyzed.* This comparison of acid and alkaline catalysis was published in full in 1907 after further work by Johnson[3] on the decrease of the conductivity of acids by the addition of esters had indicated the formation of these ester salts (I) and (M).

$$CH_3COOR + H + Cl \rightleftarrows \underset{(I)}{CH_3COOR.H} + Cl \rightleftarrows \underset{(M)}{CH_3COOR.HCl}$$

It was pointed out that the velocity of saponification is proportional to the concentration of the complex cation, (I), and therefore approximately to the product of the concentrations of the ester and the hydrogen ions, as is observed experimentally in dilute solutions. But the *possibility of the hydrolysis of the nonionized salt, (M), of esters, amides, cane sugar, etc., was also discussed very fully*[4] in several places, and *this idea differentiates our theory from all others ever proposed.* Bredig, Lapworth, Stieglitz, Goldschmidt and Acree had suggested the idea that the complex anions[5] and cations enter into chemical reactions, but *we were the first to point out clearly that the nonionized salts may also be concerned in the same reactions,*[1] *and the first to publish the correct application*[2] *of the mass law to all of these cases.*

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[1] We mean by *alkaline catalysis* the changes involving hydroxides, ethylates, phenolates, urazole salts, sulphydrates, etc., of the metals and organic bases, whether these be formed in large or small quantities.

[2] Dissertation, Johns Hopkins University, 1905–6. THIS JOURNAL, **43,** 505.

[3] THIS JOURNAL, **38,** 258.

[4] *Ibid.*, **37,** 410; **38,** 265–274, 301, 303, 306, 339, and many other articles.

[5] Kastle was undoubtedly the first to point out that in the saponification of esters and amides, and in the esterification of organic acids, the catalyzing acid forms oxonium or ammonium salts which react with the water or alcohol. He did not take up the question whether these salts undergo changes through their molecules or ions (see P. Am. Assn. Adv. Sci., **47,** 238, for an abstract of the original article, which was never published in full).

We pointed out that if (M) were the substance chiefly hydrolyzed the velocity of the reaction would be practically proportional to the product of the concentrations of the cane sugar or ester, hydrogen ions and chloride ions, or, when little organic acid is formed, to the product of the concentrations of the ester and the *square* of the concentration of the hydrogen ions, instead of the *first power* actually observed. We then wrote:[3] "It therefore follows that the undissociated salt, C_m, cannot be the substance which is chiefly undergoing hydrolysis, *although it may do so to a small extent.*" (Italics new!)

With this idea in mind we applied the theory to those cases in which the activity of the nonionized salt increases to such a "large extent" that the reaction velocity is truly practically proportional to the concentration of the nonionized salt, (M), or, for example, to the product of the concentrations of the ester, hydrogen ions and halide ions. The rearrangement of acetylchloroaminobenzene by hydrochloric acid or hydrobromic acid represents such a case:

$$\mathrm{CH_3CONClC_6H_5} + \overset{+}{\mathrm{H}} + \overset{-}{\mathrm{Cl}} \rightleftarrows \underset{\text{(M)}}{\mathrm{CH_3CONHCl_2C_6H_5}} \rightleftarrows$$

$$\mathrm{CH_3CONHC_6H_4Cl} + \overset{+}{\mathrm{H}} + \overset{-}{\mathrm{Cl}}$$

and constants were obtained which varied only a few per cent., notwithstanding the fact that the concentrations of the acetylchloroaminobenzene, C_a, hydrogen ions, C_H, and bromide ions, C_{Br}, were each varied nearly 1000 per cent., as the following table[4] shows:

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[1] This fact has been emphasized by Stieglitz, for instance, in This Journal; **39**, 402–3.

[2] For a discussion of weaknesses in the ideas of Stieglitz, Euler, Zengelis, *et al.*; see This Journal, **38**, 342; **39**, 521.

[3] This Journal, **38**, 306.

[4] *Ibid.*, **37**, 410; **38**, 265; **41**, 464.

Table V

$C_{\bullet}$	C_{Br}	C_H	K
0.00240	0.00234	0.00676	710
0.00400	0.00390	0.00770	700
0.00586	0.00565	0.00900	760
0.00780	0.00746	0.01033	740
0.01134	0.01070	0.01300	720
0.01714	0.01595	0.01760	730
0.02100	0.01940	0.02440	730

Average K = 730

The importance of this case in the study of catalysis was emphasized at that time in these words:[1] "In nearly all catalytic reactions studied heretofore, such as the hydrolysis of esters, inversion of cane sugar, hydrolysis of amides, etc., the velocity of transformation has been found to be simply proportional to the concentration of the hydrogen ions. These two different cases are very important in that they throw light on the theory of catalysis in general and in that they make it possible to determine, in cases where only a small amount of the intermediate compound or salt is present, whether the substance undergoing transformation is the undissociated salt or the ionic form of the salt."

Since that time two researches on acid catalysis have been published by Goldschmidt and by Stieglitz which show very clearly that our theory is a helpful guide for further work. In the esterification of acids and amides the reaction is catalyzed by hydrogen ions, and it has been assumed by Bredig, Lapworth, Goldschmidt, Stieglitz and Acree that the hydrogen[2] ions may combine with the organic acid or amide and form a complex cation, (I), which then unites with the alcohol and forms a complex which yields the ester:

$$CH_3COOH + \overset{+}{H} + \overset{-}{Ac} \rightleftarrows \underset{(I)}{CH_3COOH.\overset{+}{H}} + \overset{-}{Ac} \rightleftarrows \underset{(M)}{CH_3COOH.HAc}$$

$$CH_3CONH_2 + \overset{+}{H} + \overset{-}{Ac} \rightleftarrows \underset{(I)}{CH_3CON\overset{+}{H}_3} + \overset{-}{Ac} \rightleftarrows \underset{(M)}{CH_3CONH_3Ac}$$

[1] THIS JOURNAL, **38**, 267.

[2] For references see Acree and Johnson: THIS JOURNAL, **38**, 258.

But according to our theory the *nonionized salt* (M) *may also be esterified*, the velocity varying with the substances. In 1909 and 1910 Goldschmidt published some studies on (1) the esterification of formic acid, acetic acid, phenylacetic acid and butyric acid by the catalyzer trichlorobutyric acid, and on (2) the auto-esterification of mono-, di-, and trichloroacetic acids, especially in the presence of the salts of these acids, which, he showed[1] very clearly, proved that the rate of esterification is *practically* proportional to the concentration of (M). If we had known of any one of these cases, Brunel, Johnson and the writer would have interpreted them in 1904–1905 and in 1907 exactly as we do to-day, and exactly as we interpreted *then* the analogous change of acetylchloroaminobenzene, discussed above, and our theory would have had more experimental verification at that time.

A further study of the reactions in (1) and the auto-esterification of formic acid should be of the greatest interest, because there is every indication that both the complex ion (I) and the nonionized complex (M) are esterified side by side with different velocities which can easily be measured,[2] and easily calculated from our equations. The reaction velocities were lowered 65 to 75 per cent. by the addition of the aniline salt: this proves clearly that the per cent. of the reaction velocity due to (I) is much greater than that due to (M). The auto-esterification of mono-, di-, and trichloroacetic acids, with or without added salts, seems to involve practically only (M). Probably in all cases (I) and (M) react side by side. Many examples of reversible and irreversible reactions will be found, without doubt, in which it can be shown experimentally that only (I) is concerned, and others[1] in which only (M) is appreciably active: and still many others will be found in which *both* the cation (I) and the molecule (M) can easily be shown to be active, as we have reported above to be the case in some of our cases of alkaline catalysis.

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[1] Goldschmidt first considered the esterification of trichloroacetic acids as a catalysis by hydrogen ions (Ber. d. chem. Ges., **29**, 2214), the incorrectness of which was shown by Donnan (Ber. d. chem. Ges., **29**, 2422). Even though it was not till 1909, or two years after our theory appeared in full, that Goldschmidt independently proposed the same explanation "nur als eine Vermutung" (Z. Elektrochem., **15**, 6; Z. physik. Chem., **70**, 627), the writer considers all of Goldschmidt's work on oxidation and reduction, catalysis and the reactions of alkyl halides to involve *more* fundamental conceptions than any other work ever published in physico-organic chemistry.

[2] The disadvantage of this work on esterification is that Goldschmidt cannot measure the *true* concentrations of (I) and (M) and their *real* reaction velocities. We hope to overcome this difficulty in the esterification of the more strongly basic hydrazides and amides, such as $CH_3CON(CH_3)_2$, and this work will have the further advantage that no water is formed as a disturbing factor (This Journal, **41**, 468. Reid: *Ibid.*, **41**, 483).

Just as we have proven experimentally for our cases of alkaline catalysis, it is very important that our theory holds *both* for (*a*) *pure catalysis* by acids in Goldschmidt's studies of esterification and in saponification, in which only *traces* of the intermediate compounds (I) and (M) are formed, and also for (*b*) the examples in which the amount of salt formed by the acid is very large and can be accurately measured, as in Stieglitz's work, which will now be discussed.

A very important line of evidence for our theory of acid

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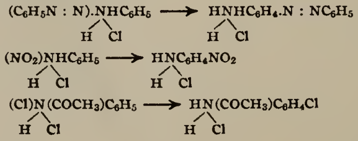
[1] In 1907 we interpreted (This Journal, **39**, 523, lines 20–21) the change of diazoaminobenzene into aminoazobenzene by aniline hydrochloride in aniline (Goldschmidt: Ber. d. chem. Ges., **21**, 1016, 2557; **25**, 1347; **29**, 1369, 1899. Z. physik. Chem., **29**, 89; **70**, 627. Ann. Chem. (Liebig), **351**, 108) as a reaction of a nonionized salt analogous to the rearrangement of acetylchloroaminobenzene by hydrochloric acid described above. Goldschmidt had previously interpreted it as a catalysis by hydrogen ions (Ber. d. chem. Ges., **29**, 1905), and later showed that perhaps the nonionized acid must be considered (Z. physik. Chem., **29**, 118). Finally, in 1910, he too came to the conclusion that it is a reaction of a *nonionized salt*, which he supposed to be the nonionized aniline salt (Z. physik. Chem., **70**, 643). Because of the equilibrium equation,

$$C_6H_5NH_2.HCl \times C_6H_5N:NNHC_6H_5 = C_6H_5N:NNH_2ClC_6H_5 \times C_6H_5NH_2 \times K$$

we reasoned that the substance transformed slowly is not necessarily the nonionized aniline hydrochloride, but perhaps the nonionized hydrochloride of the diazoaminobenzene, this kind of reaction being found quite frequently in pentavalent nitrogen derivatives. The $C_6H_5N:N-$ group, just like the other negative groups, migrates into the benzene ring in the para position:



$$(C_6H_5N:N).\underset{H\ \ Cl}{N}HC_6H_5 \longrightarrow H\underset{H\ \ Cl}{N}HC_6H_4.N:NC_6H_5$$

$$(NO_2)\underset{H\ \ Cl}{N}HC_6H_5 \longrightarrow H\underset{H\ \ Cl}{N}C_6H_4NO_2$$

$$(Cl)\underset{H\ \ Cl}{N}(COCH_3)C_6H_5 \longrightarrow H\underset{H\ \ Cl}{N}(COCH_3)C_6H_4Cl$$

The exact mechanism of all these migrations has not yet been learned, and the writer has a number of views which will be tested quantitatively. It does not seem absolutely certain, for instance, that Goldschmidt has sufficient evidence to disprove the idea that in the rearrangement of the diazoaminobenzene by aniline hydrochloride there may be a trace of the diazonium chloride present as an equilibrium constituent which reacts *reversibly* and rapidly with the amino group of the aniline, but *irreversibly* and slowly with the benzene nucleus.

catalysis is all of the fine experimental work of Stieglitz,[1] and of his collaborators, on the catalysis of imido ester salts, to which chemists should give the highest consideration. It will be recalled that Stieglitz found that the reaction is not purely that of the cation, and that he attempted to explain this deviation, or so-called "salt catalysis," by using the Arrhenius-Euler[2] hypothesis that the water reacts only through its hydrogen and hydroxyl ions,

$$C_6H_5C(:N\overset{+}{H}_2)OCH_3 + \overset{+}{H} + \overset{-}{O}H \longrightarrow C_6H_5COOCH_3 + \overset{+}{N}H_4$$

and that the cations of the salts increase the per cent. of ionization, or K_w, and hence active mass, of the water and in this way increase the velocity of the saponification. It has been pointed out by the writer[3] that this explanation probably involves a fundamental error: the error is the assumption that the water must react through its ions alone, and can change in ionization as much as is demanded by Stieglitz's explanation of his results. (1) Such an assumption, in connection with well known cases of reactions involving water directly or indirectly, leads to the contradictory conclusion that *the same cation in the same concentration must in one case* INCREASE *and in another case* DECREASE *the value of* K_w. (2) Lorenz and Böhi[4] made direct measurements of the ionization of water in the presence of various amounts of salts, acids and bases by the use of the hydrogen electrode and found values for the ionic concentration of water at 0°, 18° and 25° which agreed within 6 per cent., or within the experimental errors, with those obtained by Kohlrausch in his measurement of the conductivity of pure water. (3) Stieglitz's own experimental work gives the best evidence against the theory that the water reacts only through its ions, which are increased in concentration by added salts. The hydrochloride of ethyl iminobenzoate is a typical case and gives the constants[5] 15.4×10^{-5},

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[1] THIS JOURNAL, **39**, 29, 166, 402, 437, 586, 719. J. Am. Chem. Soc., **32**, 221.

[2] Euler: Z. physik. Chem., **32**, 348. Arrhenius: *Ibid.*, **1**, 110; **4**, 226; **31**, 197.

[3] See THIS JOURNAL, **41**, 475, for a general discussion of this question, which will be amplified in our detailed report.

[4] Z. physik. Chem., **66**, 733.

[5] Derby: THIS JOURNAL, **39**, 470–1.

136×10^{-5}, and 307×10^{-5} at 0°, 18° and 35°, respectively. When these figures are substituted in the equation[1] $K_T = K_{T_0} \times 10^{(T-T_0)C}$ we find the values $C = 0.0525$ and $C = 0.0520$, for the intervals 0°–18° and 0°–25°, respectively. These are perfectly normal values for C, about like our value $C = 0.0526$ for the reaction of methyl iodide and sodium phenolate, for instance. Since, however, K_w for water at 0°, 18° and 25° is about 0.12×10^{-14}, 0.64×10^{-14} and 1.2×10^{-14}, respectively, the reaction velocities 136 and 307 must be divided by 5.3 and 9.6 to make equal and comparable the factor for the ionized mass of the water at 0°, 18° and 25°. When this is done, we find for the intervals 0°–18° and 0°–25° the values $C = 0.0120$ and $C = 0.0127$, respectively, which *are* LESS THAN ONE-FOURTH THE NORMAL VALUE *0.0526 found in our reactions, for instance.* To state it another way, if the reaction velocities of imido ester salts actually have normal temperature coefficients and his interpretation is correct, then Stieglitz should have found values at 18° and 25° which, compared with those found at 0°, were 5.3 and 9.6 times as large as those actually observed. In the light of these three lines of evidence the interpretation given by Stieglitz to these phenomena appears to the writer to be plainly untenable.

Now all the *published* work of Stieglitz and his coworkers fits our theory very nicely, and gives excellent evidence, without any faulty assumptions, that both the imido ester cations and the nonionized imido ester salts are saponified in the following way:

$$C_6H_5C(:\overset{+}{N}H_2)OC_2H_5 + H_2O \longrightarrow C_6H_5COOC_2H_5 + \overset{+}{N}H_4$$
$$C_6H_5C(:NH_2Cl)OC_2H_5 + H_2O \longrightarrow C_6H_5COOC_2H_5 + NH_4Cl.$$

By using Stieglitz's latest values,[2] Dr. C. N. Myers has found for the benzimidonium ethyl ester chloride, bromide and nitrate the figures $K_i = 162$ and $K_m = 50.3$, $K_i = 163.8$ and K_m 46.5, $K_i = 163.2$ and $K_m = 48.2$, respectively. These values of K^i are identical within the experimental errors; they should be identical because all three salts yield the same cation.

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[1] Hecht and Conrad: Z. physik. Chem., **3**, 465.

[2] J. Am. Chem. Soc., **32**, 224.

Not only does our theory interpret his experimental results properly when the imido ester salt alone is hydrolyzed, but also, as far as we can calculate from his published results, when added hydrochloric acid, potassium chloride, potassium bromide, lithium chloride, etc., increase the "salt effect." Stieglitz wrote:[1] "We arrived thus *empirically at the rather unexpected result* (italics ours) that the accelerating factor A is approximately the same for the sodium, potassium and lithium chlorides and for the bromides as well as for the chlorides, viz., about 185 per cent. per gram molecule of fully ionized salt." But these facts, instead of being "empirical" and "rather unexpected" to us, were *predicted* from our theory, since the per cent. of ionization and hence reaction velocity of the imido ester salt would be the same in all of these cases. Our theory gives, then, a perfecty rational explanation of their so-called "salt effect" and proves it to be "normal"[2] and due *chiefly*, as in our work, *to the reaction of the nonionized imido ester salt, which Stieglitz did not take into consideration in his theory.*[3] Dr. C. N. Myers and the writer will soon publish in a separate article all of the mathematical details of this new interpretation of the reactions of imido esters.

Since the reactions of Stieglitz and his coworkers have nearly normal temperature coefficients it is evident that their work proves the water to react *chiefly* through its molecules,[4]

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[1] J. Am. Chem. Soc., **32**, 223.

[2] At the New York meeting of the Int. Cong. Appl. Chem. Professor Stieglitz reported that his unpublished and most accurate data on the effect of added salts show that there is a deviation, or, as we say, an "abnormal salt effect," analogous to that found in some of our reactions.

[3] We called attention four years ago to the possibility of the reaction of the nonionized imidoester salt (THIS JOURNAL, **39**, 521).

[4] When the mass law holds for the reactions

$$C_6H_5C(:\overset{+}{N}H_2)OCH_3 + H_2O \rightleftarrows C_6H_5C(:NH)OCH_3 + H_2O.\overset{+}{H}$$

$$C_6H_5C(:NH_2Cl)OCH_3 + H_2O \rightleftarrows C_6H_5C(:NH)OCH_3 + H_2O.HCl$$

it is impossible to tell from the data whether the products on the left of the arrows or the ones on the right, or both, yield the end products (Acree: THIS JOURNAL, **39**, 302. Goldschmidt and Sunde: Ber. d. chem. Ges., **39**, 711. Goldschmidt and Udby: Z. physik. Chem., **60**, 728). We shall consider only the compounds on the left in our interpretation because nothing is known about the ionization of $H_2O.HCl$, and because Stieglitz's values for the ionization and reaction velocities of the imido ester salts harmonize with our theory.

as discussed in the preceding section (3). We may assume the ions of the water to enter into these changes to a certain extent, which may be determined by the *difference* between the *observed* temperature coefficient and the *real* temperature coefficient of the reaction between *given concentrations* of the imido ester cation, nonionized salt, hydrogen ions and hydroxyl ions. This same reasoning could be applied to a large number of cases of reactions of water and analogous substances, in order to learn to what extent the ions and the molecules of the substance are concerned in the changes, provided the necessary experimental data can be secured.

PHYSICAL CATALYSIS

The question how the particles come together before reaction takes place is very important. We have for several years believed with Michael and others that the alkyl halide may actually combine with the phenolate anion, for example, (or sodium phenolate molecule), and form at least a trace of a highly reactive complex ion (or molecule). Expressed in the ideas of J. J. Thomson, it may be that the alkyl halide and phenolate anion must come close enough together to allow an interchange or disturbance of electrons.[1] In the same way a mechanical disturbance, or a disturbance of the electrons through "electrostatic induction" by the electrolytes[2] present, might so change the arrangement of the atoms and electrons of a molecule of alkyl halide and of another sodium phenolate that a point of one molecule would, *in effect*, become momentarily negative and a point of the other positive:[1] hence the two could combine electrically and react further. Perhaps the molecules can combine without any such electronic disturbance or transfer; J. J. Thomson says[2] that "We thus see that it is possible to have forces electrical in their origin binding the two systems together without a resultant charge on either system," and this idea may be extended to molecules. Substantial evidence for such an idea was found in the isolation and study of Scholl[3] and Steinkopf's double compound of silver nitrate and cyanomethyl iodide, which was found to change readily in the solid state or in solution into cyanomethyl nitrate and silver iodide.

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[1] For central ideas in this connection see: J. J. Thomson: "The Corpuscular Theory of Matter", pp. 120–141 (1907). Science, **30**, 257. Fry: Z. physik. Chem., **76**, 385–397; 398–412. J. Am. Chem. Soc., Proceed., **30**, 34. *Ibid.*, **34**, 664. Falk and Nelson: J. Am. Chem. Soc., **32**, 1637–1654; **33**, 1140. School of Mines Quarterly, **30**, 179–198. For some interesting applications see L. W. Jones: THIS JOURNAL, **48**, 25–27. For a very suggestive discussion see L. G. Winston. THIS JOURNAL, **45**, 547. For a comprehensive report see W. W. Strong: THIS JOURNAL, **44**, 85. See Nef: J. Am. Chem. Soc., **26**, 1549; **30**, 645, for very important ideas connecting his theory of bivalent carbon with a practical equivalent of the electron theory. Julius Meyer: Z. physik. Chem., **66**, 81; **67**, 257. Kraus: J. Am. Chem. Soc., **29**, 1557; **30**, 653, 1197, 1323.

[2] J. J. Thomson: "The Corpuscular Theory of Matter", p. 135. L. G. Winston: THIS JOURNAL, **45**, 547. This idea of a *physical catalysis* by electrolytes was proposed by the writer in 1908 and 1909 (THIS JOURNAL, **39**, 308–9). "..... *a catalyzer may influence the velocity of a reaction physically* .... by imparting energy to, or removing it from, the system." (*Ibid.*, **41**, 483): "Finally, one other salt effect must be considered. The thermodynamic potential, or 'activity,' or driving force behind each reaction depends not only upon the substances themselves but upon the surrounding *field*. When this is changed by the addition of electrolytes or nonelectrolytes there will be a change in the corresponding thermodynamic potential and therefore in the reaction velocity, although this will in many cases be negligible." It may be negligible in the dilute solutions and become more and more noticeable, if at all, as the concentration increases.

In developing the equations which we should use we may consider the case first in which the alkyl halide reacts with the phenolate anion. If these unite to form a complex anion in very small traces and we represent the concentrations by the formulas, the equation

$$(a)\ CH_3I \times An = K \times CH_3I.An$$

holds approximately for any given concentration even though the value of the "stability constant" K is not constant for all concentrations. We cannot measure K experimentally at present and our only reason for thinking that K should remain constant for nearly all concentrations is that the applica-

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[1] This idea was proposed in 1908 (address at the Baltimore meeting of the A. A. A. S., December, 1908. Science, **30**, 624) to explain, for instance, the addition of chlorine or hydrogen to ethylene,

$$CH_2 : CH_2 + Cl_2 \longrightarrow \overset{+}{C}H_2.\overset{+}{C}H_2 + 2\overset{-}{Cl} \longrightarrow C_2H_4Cl_2$$

We suggested at that time the use of electromotive force methods to study this and similar problems, and since then Dr. L. J. Desha, Dr. N. E. Loomis, and Dr. C. N. Myers have made a number of measurements of the sytems $Pt—H_2—HCl—C_2H_4—Pt$, $Pt—Cl_2—HCl—C_2H_4—Pt$, and $Pt—O_2—NaOH—C_2H_4—Pt$. In all of these cases we have secured rather constant values, which range from 0.55 volt to 0.85 volt. We shall not feel justified in publishing the data until we can prepare *very pure ethylene* and prove beyond question that the electromotive force truly represents the above reactions, and does not arise from small traces of oxygen and other impurities in the ethylene.

[2] "The Corpuscular Theory of Matter", pp. 121, 127, 130 and 135.

[3] Ber. d. chem. Ges., **39**, 4393. Hantzsch and Caldwell: *Ibid.*, **39**, 2472. Acree and Loy : THIS JOURNAL, **45**, 224.

tion of the mass law has shown that the stability constants of most complex salts, such as double cyanides, complex ammonium salts, etc., are fairly constant. If this complex yields the end products the following equations hold approximately, whether the complex salt is formed slowly (either reversibly or irreversibly) and decomposes rapidly, or is formed rapidly reversibly and decomposes slowly:

$$\begin{aligned}(b)\quad \frac{dx}{dt} &= K'_i \times CH_3I.An \\ &= K'_i /K \times CH_3I \times An \\ &= K_i \times CH_3I \times An\end{aligned}$$

But this is exactly the equation that we get if the alkyl halide and anion react directly without the formation of an intermediate complex anion. In the one case our reaction velocity constant $\frac{K_i}{K}$ is the quotient of two constants, both of which (or the quotient) are assumed to be constant for all concentrations: in the other case we make no *assumptions* other than the constancy of the reaction velocity K_i, the validity of which assumption is tested experimentally.

In the present studies, however, the above equation fails to represent the entire reaction, and we may therefore consider the possibility of the reactions of nonionized substances. It might well be that the *nonionized* double salt,

$$CH_3I.NaOC_6H_5,$$

can decompose *in solution* into sodium iodide and phenyl methyl ether just as we have shown the *solid* (and presumably *nonionized*) cyanomethyl iodide-silver nitrate double compound to yield silver iodide and cyanomethyl nitrate. We may consider this nonionized double salt to be formed by the union of the alkyl halide with the sodium ions and phenolate ions, or by the union of the alkyl halide with the nonionized sodium phenolate. These two processes are represented as follows:

$$(c)\quad CH_3I \times \overset{-}{O}C_6H_5 \times \overset{+}{Na} = K' \times CH_3I.NaOC_6H_5, \text{ and}$$

$$(d)\quad CH_3I \times NaOC_6H_5 = K'' \times CH_3I.NaOC_6H_5$$

It is clear that if sodium phenolate obeyed Ostwald's dilution law, and the equation

$$\overset{+}{Na} \times \overset{-}{OC_6H_5} = K''' \times NaOC_6H_5 = \frac{K'}{K''} \times NaOC_6H_5$$

were true for all concentrations, K' and K'' also being constant, we could not possibly tell which of these two processes is taking place. The reaction (*c*) would be written

$$(e)\quad \frac{dx}{dt} = K'_m \times CH_3I.NaOC_6H_5$$
$$= \frac{K'_m}{K'} \times CH_3I \times \overset{-}{OC_6H_5} \times \overset{+}{Na}$$
$$= \frac{K'_m K'''}{K'} \times CH_3I \times NaOC_6H_5$$
$$= \frac{K'_m}{K''} \times CH_3I \times NaOC_6H_5 = K_m \times CH_3I \times NaOC_6H_5$$

The reaction (*d*) would be written:

$$(f)\quad \frac{dx}{dt} = K'_m \times CH_3I.NaOC_6H_5$$
$$= \frac{K'_m}{K''} \times CH_3I \times NaOC_6H_5 = K_m \times CH_3I \times NaOC_6H_5$$

which would also hold true even if no complex salt were formed as an intermediate product. If the sodium phenolate obeyed the Ostwald dilution law these two equations could be used interchangeably and we could not know whether the sodium phenolate reacts through the sodium and phenolate ions together, or through its nonionized portion, or through both processes together, and we could not know whether a trace of the complex salt is an intermediate product. Sodium phenolate does not obey the Ostwald dilution law and these equations (*e*) and (*f*) are not identical by any means. If equations (*b*) and (*c*) represent the true reactions the total reaction can be represented by the equation (*g*) if α is the ionization, and $(A-x)$ is the concentration of the sodium phenolate, and $(B-x)$ is the concentration of the alkyl halide, at the time t, and x is zero when t is zero.

$$(g)\quad \frac{dx}{dt} = K_i\alpha(A-x)(B-x) + K_m\frac{\alpha^2}{V}(A-x)(B-x)$$

$$= \left[K_i\,\alpha + K_m\,\frac{\alpha^2}{V}\right](A-x)(B-x),\ \text{or}$$

$$K_V = K_i\,\alpha + K_m\,\frac{\alpha^2}{V} = \frac{B}{t(A-B)}\,\text{logn}\,\frac{B(A-x)}{A(B-x)}$$

Equation (*h*) holds true if equations (*b*) and (*f*) represent the two side reactions:

$$(h)\quad \frac{dx}{dt} = K_i\alpha(A-x)(B-x) + K_m(1-\alpha)(A-x)(B-x)$$

$$= [K_i\alpha + K_m(1-\alpha)]\,(A-x)(B-x),\ \text{or}$$

$$K_V = [K_i\alpha + K_m\,(1-\alpha)] = \frac{B}{t(A-B)}\,\text{logn}\,\frac{B(A-x)}{A(B-x)}$$

If we inspect equations (*g*) and (*h*) carefully we see that they become more and more nearly identical as the salt comes closer and closer to obeying the Ostwald dilution law, as pointed out above. When they become nearly, or quite, identical the values of K_V, K_i and K_m in both equations (*g*) and (*h*) become nearly or quite *constant*, within the experimental errors, and hence it is impossible to decide, from the equations alone, which of the two interpretations of the reaction is correct. If we inspect equation (*g*) closely we see that it has the same form as the one demanded by the Arrhenius-Euler theory of salt catalysis which Stieglitz has used so successfully in his fine work on the imido esters, and this fact accounts for his success in obtaining any constants at all in his work. *When equation (g) is applied to our work we secure constants in only two cases,*[1] *but equation (h) gives satisfactory constants in every case studied by us up to this time, and also in all of Tubandt's, Goldschmidt's, and Stieglitz's published work. For that reason we believe that we have secured valid evidence for the theory that we must consider the possibility of the reactions of both ions and molecules in all reactions.* Whether in the two particular cases mentioned the alkyl halide does actually react with both ions together, perhaps along with the nonionized molecules, or whether it is a case of an "arithmetical accident" cannot be said at present.

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[1] Even certain corrections for fluidity have not aided us.

We are presenting our results merely in the light of what has been accomplished. We are studying the effect of physical factors such as viscosity and fluidity, and are extending the investigations to solutions more dilute than N/64 and hope that we shall be able to investigate some of them as dilute as N/1024. If the theory is found to hold over the entire range from N/1 to N/1024, even in the presence of added salts, we shall then feel that we have a working hypothesis by which to study all reactions. In some other cases, as pointed out before,[1] it may be found that the main reaction is disturbed, or that a so-called "abnormal salt catalysis" is produced, on account of an electronic disturbance, or of the formation of still other complex compounds, in *traces* in some cases, the ions or molecules of which have reaction velocities greater or smaller than those of the original constituents. The formulas

$$CH_3I.C_2H_5ONa.NaI,\ \ CH_3I.C_2H_5ONa.\overset{+}{Na}\ \ \text{and}$$
$$C_6H_5C(:NH_2Cl)(OC_2H_5).KCl$$

are illustrations, and the variations of this central idea are manifold.

In Table VI are given the values of K_i and K_m found in the work in this laboratory, while in Table VII are given the values of K_i and K_m which we have calculated from the work of other investigators:

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[1] For references see Acree: This Journal, **41**, 475.

Table VI

Reaction	Observer	K_i	K_m
(1) Sodium ethylate and methyl iodide at 25°	Dr. H. C. Robertson	0.127 [1]	0.0594
(2) The same	Miss B. Marion Brown	0.1294	0.0573
(3) Potassium ethylate and methyl iodide at 25°	Dr. Julia P. Harrison	0.127	0.066
(4) Sodium ethylate and ethyl iodide at 25°	Dr. E. K. Marshall	0.0120	0.00427
(5) The same	Mr. J. H. Shrader	0.0122	0.00404
(6) Sodium ethylate and ethyl bromide at 25°	Dr. E. K. Marshall	0.00576	0.00233
(7) Sodium phenolate and methyl iodide at 25°	Dr. H. C. Robertson	0.0282	0.00474
(8) Potassium phenolate and methyl iodide at 25°	Dr. H. C. Robertson and Mr. J. H. Shrader	0.0283	0.0037
(9) Lithium phenolate and methyl iodide at 25°	Dr. H. C. Robertson and Mr. J. H. Shrader	0.0284	0.0040
(10) Sodium phenolate and methyl iodide at 25°	Dr. H. C. Robertson	0.091	0.0131
(11) Sodium phenolate and ethyl iodide at 25°	Dr. H. C. Robertson	0.0056	0.00099
(12) The same at 35°	Dr. H. C. Robertson	0.0184	0.00323
(13) Sodium phenylthiourazole and ethyl iodide at 25°	Dr. J. Chandler	0.465	0.16
(14) The same (in aqueous alcohol) at 25°	Dr. Sidney Nirdlinger and Dr. F. M. Rogers	0.43	0.17
(15) Sodium ethylate and acetimido ethyl ester at 25°	Dr. E. K. Marshall	0.344	0.228
(16) Sodium ethylate and benzimido ethyl ester at 25°	Dr. Julia P. Harrison	0.1148	0.1003
(17) Acetylchloroaminobenzene and hydrobromic acid at 3°	Dr. J. M. Johnson	Very small	730

[1] The values in brackets should be, and are, practically identical. K_i and K_m involve in some cases a small "abnormal salt effect" which will be discussed in the final report.

Table VII

Reaction	Observer	K_i	K_m
(18) Inversion of menthone by sodium ethylate	C. Tubandt	0.41 at 20° 0.93 at 30°	0.41 at 20° 0.93 at 30°
(19) Rearrangement of diazoaminobenzene into aminoazobenzene by aniline hydrochloride in aniline at 25°, and many other similar examples	H. Goldschmidt	Very small	0.06
(20) Auto-esterification of trichloroacetic acid in absolute ethyl alcohol at 25°	H. Goldschmidt	Very small	0.026
(21) Esterification of acetic acid by trichlorobutyric acid in the presence of its aniline salt in absolute ethyl alcohol at 25°	H. Goldschmidt	Ionic reaction suppressed by aniline salt	About 0.0073 for 1.0 N trichlorobutyric acid
(22) Esterification of phenylacetic acid by trichlorobutyric acid in the presence of its aniline salt in absolute ethyl alcohol at 25°	H. Goldschmidt	Ionic reaction suppressed by aniline salt	About 0.00055 for 1.0 N trichlorobutyric acid
(23) Esterification of *n*-butyric acid by trichlorobutyric acid in the presence of its aniline salt in absolute ethyl alcohol at 25°	H. Goldschmidt	Ionic reaction suppressed by aniline salt	About 0.0038 for 1.0 N trichlorobutyric acid

Table VII—(Continued)

Reaction	Observer	K_i	K_m
(24) Esterification of formic acid by trichlorobutyric acid in the presence of its aniline salt in absolute ethyl alcohol at 25°	H. Goldschmidt	Ionic reaction suppressed by aniline salt	About 0.125 for 1.0 N trichlorobutyric acid
(25) Saponification of benzimidonium ethyl ester chloride at 25°	J. Stieglitz	162.0 [1]	50.3
(26) Saponification of benzimidonium ethyl ester bromide at 25°	J. Stieglitz	163.8	46.5
(27) Saponification of benzimidonium ethyl ester nitrate at 25°	J. Stieglitz	163.2	48.2
(28) A number of other reactions described by Stieglitz and his coworkers, at other temperatures, and in the presence of various salts, hydrochloric acid, etc.	J. Stieglitz and coworkers	......	......
(29) Change of benzaldehyde into benzoin by potassium cyanide	Bredig and Stern	About 0.089	About 0.089

[1] The values in brackets should be, and are, practically identical. The values are given in terms of Stieglitz's constants.

Johns Hopkins University
September 1, 1912

OBITUARY

PAUL ÉMIL LECOQ DE BOISBAUDRAN[1]

Paul Émil Lecoq de Boisbaudran, the discoverer of the element gallium, died in Paris on May 28, 1912. He was born at Cognac, Charente, on April 18, 1838, and was therefore 74 years old at the time of his death. His early education was entirely neglected and at the age of 15 he entered the employ of his father, who conducted a liquor store. He devoted all his spare time to scientific studies, however, and finally secured a place in the laboratories of the University of Paris. Here he remained three months, casting longing eyes on the collection of rare earths gathered there but to which he was denied access on account of his inexperience and deficient preparation. He then went to Würtz in the École de Médecine, and it was here, in 1875, that he discovered gallium in a Pierrefitte blende.

He never occupied any official position and all his work was done without help from assistants or students. The results of his investigations were published in numerous short isolated articles and many have therefore not secured the attention and recognition which they deserve.

In 1876 he was awarded the Cross of the Legion of Honor for his discovery of gallium. In 1872 the Paris Academy of Sciences voted him the Bordin Prize and in 1880 the La Caze Prize. Two years earlier he had been elected Corresponding Member. In 1879 he was given the Davy Medal.

The last years of his life were spent in La Combe and in Paris where, in a small private laboratory, he devoted all his leisure time to his investigations.

While his scientific activities were many-sided, including such subjects as gravity, meteorology and problems in agricultural chemistry, he was preëminently a physical chemist and he stands by the side of Kirchhoff, Bunsen and Sir W. Crookes as one of the founders of Spectrochemistry. In this connection may be mentioned the relations, first pointed out by him, between the spectra of elements and their atomic weights, and the development of the method for the investigation of the spark spectra of solutions. This method led to his discovery of gallium, a discovery which fitted in so brilliantly with Mendeléef's system, although Lecoq de Boisbaudran's work was in no wise suggested by this theory. Attention should also be called to his investigations on cathodic phosphorescence phenomena which involved the idea of solid solutions, now generally considered quite a modern conception; on the applications of electrolysis to chemical analysis; and on supersaturation. The work to which he devoted the greater part of his life and which is best known is, of course, that on the rare earths, in the course of which he discovered two other new elements, samarium and dysprosium.

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[1] This note is based on an admirable sketch by Prof. G. Urbain in the Chem. Ztg., **36**, 929–933.

REVIEWS

Messungen elektromotorischer Kräfte galvanischer Ketten mit wässerigen Elektrolyten. Gesammelt und bearbeitet im Auftrage der Deutschen Bunsen-Gesellschaft von R. Abegg, Fr. Auerbach, R. Luther. Halle a. S.: Verlag von Wilhelm Knapp. 1911. Price, M. 8.40.

No man interested in electrochemistry can afford to be without this book. The first part deals with the literature on electromotive-force measurements in aqueous solutions and contains nearly all references of any value. The second part deals with the experimental data obtained by various workers, and the third part gives the electrode potentials arranged according to elements and also according to increasing values. The names of the authors are a guarantee of the importance of this volume.

S. F. Acree

Outlines of Organic Chemistry. A Book Designed Especially for the General Student. By F. J. Moore, Ph.D., Associate Professor of Organic Chemistry in the Massachusetts Institute of Technology. New York: John Wiley & Sons; London: Chapman & Hall, Limited. 1910. pp. v + 315. Price, $1.50.

This book was designed to meet the needs of students specializing in Physics, Biology and Sanitary Engineering. For that reason the author has omitted several important subjects, such as the acetoacetic ester synthesis, the Grignard reaction, and *cis-trans* isomerism. All of the classes of compounds taken up, however, are of the greatest economic and scientific value, and the treatment of these subjects is clear and interesting. The reviewer finds especially praiseworthy the constant use of the graphical formula, the chapter on amino acids and proteins, and that on the organic chemistry of vital processes.

S. F. Acree

ERRATUM

Plates VIII and X, facing pp. 117 and 119, should be interchanged.

VOL. XLVIII NOVEMBER, 1912 No. 5

AMERICAN

CHEMICAL JOURNAL

THE COPPER COMPLEXES OF AMINO ACIDS, PEPTIDES AND PEPTONES[1]

II. THEIR CONFIGURATIONS AND RELATION TO THE BIURET REACTION

BY P. A. KOBER AND K. SUGIURA

I. The Formulas and Configurations
II. Valency of Protein Nitrogen
III. Biuret Reaction for Proteins
IV. A Review of Previous Work on Allied Compounds
V. General Discussion and Conclusions
VI. Experimental

I. THE FORMULAS AND CONFIGURATIONS

In our first paper[2] we show that monobasic α-amino acids, without exception, form complex copper salts with the general formula CuA_2, where A represents a monobasic α-amino acid. Where the amino group is in the β position, the formula is the same except that when, as in isoserine, there is a hydroxyl group in the α position, the formula is CuA. With dibasic amino acids like glutaminic, aspartic and cystinic, the formula is CuA, where A represents one molecule of a dibasic amino acid.

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[1] Read in part before the Section on Organic Chemistry, International Congress of Applied Chemistry, New York, 1912.

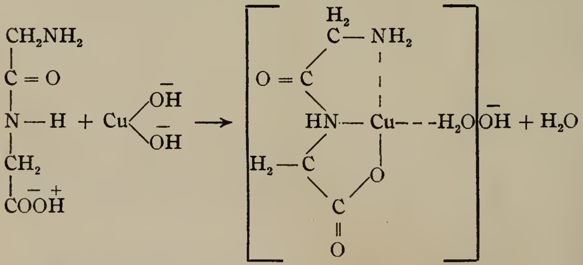
[2] J. Biol. Chem., 13, 1 (1912).

Fischer[1] found that other amino acids, where the NH_2 group was in the γ, δ or ε position, regardless of a hydroxyl group in the α position, did not form complex copper salts.

Our results on 50 polypeptides, whose copper salts were soluble, corroborate those of Fischer and Abderhalden on 5 isolated peptide copper salts, which have the general formula $(\text{peptide})_1Cu_1$. In other words, the results show unmistakably that one molecule of peptide, whatever number of amino acids it may contain, combines with only one molecule of copper hydroxide.

The questions that remain to be solved are: How are these copper salts formed and what is their structure?

Taking glycylglycine for an example: It is interesting to attempt to picture the structure of this peptide, keeping in mind the latest work of Werner on the valency of nitrogen.



One statement we can, without much doubt, assume to be correct, namely, that one hydroxyl group is neutralized by the hydrogen of the carboxyl group, as in the case of ordinary salt formation. Although lack of material prevented our making accurate calorimetric experiments, yet comparative heats of formation of copper acetate, copper glycine and copper glycylglycine were determined.[2] Using 0.01 of a mole we found slightly less heat evolved from copper glycine than from copper acetate, and the heat from copper glycylglycine is about half of that from copper glycine. This is consistent with the equation just given. Of course we are not certain

[1] Ber. d. chem. Ges., **42**, 4883 (1909).

[2] See experimental notes, p. 410.

that the heat of formation of copper glycylglycine should be equal to the heat of neutralization. It may be more or decidedly less.

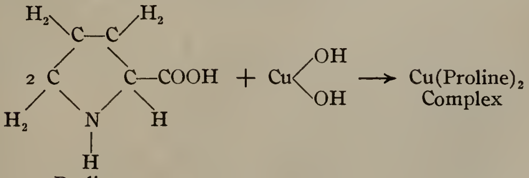
The other hydroxyl group now remains to be placed, or, in other words, it is necessary to locate the position of the other principal copper valence.

The imino group alone does not seem to be sufficient to form a copper salt. Thus bromo or chloro derivatives of dipeptides, as well as hippuric acid, and formyl derivatives of amino acids, all having an imino group but no amino group, do not form these complex copper salts with copper hydroxide.

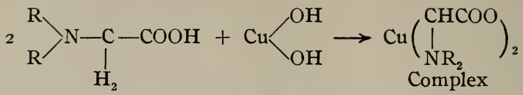
We examined the following substances with our technic, but found no complex salts in neutral solutions:

Chloroacetylalanine
Chloroacetylaminobutyric acid
Chloroacetylvaline
Chloroacetyl-*l*-leucine
Chloroacetyl-*l*-tyrosine
Bromopropionylglycine
Bromopropionyl-*d*-alanine
l-Bromopropionyl-*d*-alanine
l-Bromopropionyl-*l*-alanine
Bromobutyrylglycine
Bromovalerylglycine
Bromoisocaproylglycine
n-Bromocaproylglycine
Bromocaproylleucine
d-Bromoisocaproyl-*d*-leucine
Formylalanine
Formyl-*d*-leucine
Formyl-*l*-tyrosine
Hippuric acid
Benzoyl-*d*-leucine

These facts show a decided difference between an $R—NH_2$ and $R—\overset{O}{\overset{/\!/}{C}}—NH—$ group, particularly when there are no other nitrogen atoms in the compound. When, however, positive radicals such as $CH_3—$, $C_2H_5—$, etc., take the place of one or more of the hydrogen atoms of the amino group, the property of forming complexes is unimpaired, e. g.,



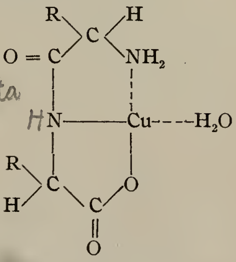
Proline



R being H, CH_3, C_2H_5, C_3H_7, etc.., as in sarcosine, diethylglycine, diethylalanine, etc.

As we mentioned before, an amino group in the γ, δ or ε position will not form a complex salt,[1] because it seems that if a salt contains a ring of seven or more members it is unstable. Werner,[2] Pfeiffer,[3] L. Tschugaeff,[4] Blau,[5] Dittley[6] and Piloty and Schlenk,[7] have found that only five- or six-membered rings in metallic complexes are stable. Therefore we may assume that for di- and tripeptides the free amino group is essential, directly or indirectly, to the formation of copper salts (see page 396); and without deciding on all questions of valence, the structure of a dipeptide copper salt is probably as follows:

see errata p. 575



(all rings five-membered)

(NOTE.—Dotted lines here represent the secondary valences of copper.)

Bromo, chloro, and other derivatives of tripeptides, which have two imino groups but no amino groups, also give very little of the copper salt with our technic in neutral solution. The tables below show this in the second and third columns.

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[1] Fischer and Zemplén: Ber. d. chem. Ges., **42,** 4883 (1909).

[2] Werner: Neuere Untersuchungen, **8,** 280 (1911).

[3] Pfeiffer and Hannan: Ber. d. chem. Ges., **36,** 1065 (1903).

[4] L. Tschugaeff: *Ibid.*, **39,** 3197 (1906).

[5] Blau: Monatsh. Chem., **19,** 690 (1898).

[6] Dittley: Ann. Chem. (Liebig), **341,** 300 (1906).

[7] Schlenk: Uber Metal-Isobutyradine und ihre Salze; Inaug.Dissert., München, **1905.**

Bromotripeptides

Substance	Weight of sample Grams	CuO in filtrate without alkali Grams	Complex color	CuO in filtrate after adding 20 cc. N NaOH Grams	Color	Theoretical weight of CuO, calculated for this sample Grams	Per cent. of theoretical of CuO in alkaline filtrate for formula $(\text{peptide})_1\,\text{Cu}_1$
Bromoisocaproylglycylglycine	0.1008		none	0.0083	complex	0.0259	32.0
Bromo-*n*-caproylglycylglycine	0.1001		none	0.0175	complex	0.0258	67.8
Bromobutyrylglycylglycine	0.0982		none	0.0218	complex	0.0278	78.4
Bromoisocaproylleucylleucine	0.1012		none	0.0060	complex	0.0191	31.4
Bromovalerylglycylglycine	0.0613		none	0.0052	complex	0.0165	31.5
d-Bromocaproylglycyl-*d*-alanine	0.0558		none	0.0092	complex	0.0137	67.2
d-Bromocaproyl-*d*-alanyl-*d*-alanine	0.0514		none	0.0073	complex	0.0121	63.3
Bromopropionylglycylglycine	0.1009		none	0.0230	complex	0.0301	76.4

Chlorotripeptides

Substance	Weight of sample Grams	CuO in filtrate without alkali Grams	Complex color	CuO in filtrate after adding 20 cc. N NaOH Grams	Color	Theoretical weight of CuO, calculated for this sample Grams	Per cent. of theoretical of CuO in alkaline filtrate for formula $(\text{peptide})_1\text{Cu}_1$
Chloroacetylglycylleucine	0.0712		none	0.0164	complex	0.0214	76.6
Chloroacetyl-*l*-alanylglycine	0.0708		none	0.0207	complex	0.0252	82.1
Chloroacetylglycylvaline	0.0924		none	0.0230	complex	0.0294	78.2
Chloroacetylglycylglycine	0.1018	0.0164 bluish green filtrate	none	0.0317	complex	0.0388	81.7
Chloroacetylleucylglycine	0.1008		none	0.0190	complex	0.0302	62.9
Chloroacetylglycylalanine	0.1012	0.0139 bluish green filtrate	none	0.0293	complex	0.0362	80.9
Chloroacetylglycylasparagine	0.1003		none	0.0199	semibiuret color	0.0300	66.3
Chloroacetylvalerylglycine	0.1004		none	0.0157	complex	0.0319	49.2

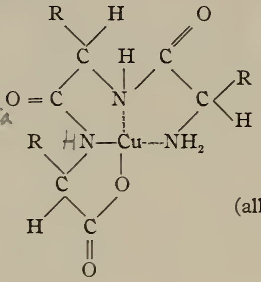
Bromotetrapeptides

Substance	Weight of sample Grams	CuO in filtrate without alkali Grams	Complex color	CuO in filtrate after adding alkali Grams	Color	Theoretical weight of CuO, calculated for this sample Grams	Per cent. of theoretical of CuO in alkaline filtrate for formula (peptide)$_1$ Cu$_1$
Bromo - *n* - caproyldi - glycylglycine	0.1018		none	0.0185	semibiuret	0.0222	83.3
Bromoisocaproyldiglycylglycine	0.0532		none	0.0109	semibiuret	0.0116	94.0
Bromovaleryldiglycylglycine	0.1008	0.0048 bluish green filtrate	none	0.0224	semibiuret	0.0228	98.2
Bromopropionyldiglycylglycine	0.0572		none	0.0133	semibiuret	0.0140	95.0
Bromobutyryldiglycylglycine	0.0506		none	0.0113	semibiuret	0.0119	95.0
"Bromocaproylpeptone"	0.1007		none	0.0113	biuret		

In alkaline solution, however, quite appreciable amounts of complex copper salts were formed and a possible reason for this will be discussed on page 396.

Here, too, the solubility of copper hydroxide in neutral solution is dependent to a large extent upon the presence of a free amino group, which serves to produce a stable ring formation,

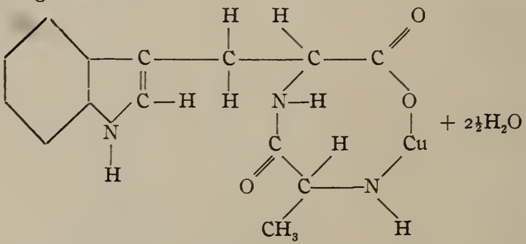
see errata p.575



(all rings five-membered)

These facts would seem to indicate that the free NH_2 group is necessary for the neutralization of the second OH group. For di-, tri- and tetrapeptides this is true; the NH_2 group or its alkyl derivative is essential to the formation of "neutral" complexes, but, as we hope to show later, only indirectly.

The only attempt to picture one of these copper salts was made by Abderhalden,[1] who gave alanyl-*l*-tryptophan the following structure:



Thus one of the hydrogen atoms of the amino group is supposed to be neutralized by the second OH ion of the copper, and an eight-membered ring is formed. Aside from the improbability of the formation of such a ring, it seems to us doubtful that, as this conception holds, the NH_2 group should be no longer basic, should form no salts such as hydrochlorides, but should on the contrary have a replaceable hydrogen atom. These peptides do form hydrochlorides, give off very little heat in forming copper salts, and in a study of the valences involved there is found no reason to believe that the hydrogen of the NH_2 group is replaceable. Nitrous acid acts (Van Slyke's method) fully as well on the free amino nitrogen of these peptides as on that of the amino acids, and according to Abderhalden's conception there is no reason why the free amino acids should not act as dibasic acids also. But this is contrary to many facts.

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[1] *Loc. cit.*

These considerations, together with facts cited in reference to ring formation, lead us to believe that in peptides, as in the free amino acids themselves, only the secondary valences of copper are connected with the amino (NH_2) group.

We are therefore forced to the conclusion *that in peptides the imino group is instrumental in combining with the second OH ion of the copper.* There is some evidence to support this. The tables given above show that bromo and chloro acid *derivatives of amino acids*, with only one imino nitrogen and no amino nitrogen, give practically *no complex*[1] *copper* salts *in neutral or alkaline solution*, while *similar derivatives of dipeptides* with two imino nitrogens dissolve no copper to form complexes in neutral solution, but in *excess of hydroxyl ions* tend to dissolve *one molecule of copper hydroxide. Similar derivatives of tripeptides* with three imino nitrogens also give no appreciable amount of complex in neutral solution, but *with alkali also give a complex (involving one molecule of copper hydroxide) which is macroscopically of the same color as alkaline tripeptide salt, suggesting a biuret color.* In these substances we can substitute the free NH_2 group and yet produce the same effects. How is this to be explained?

---

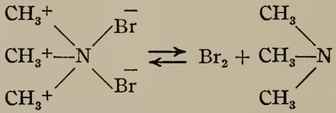
[1] A trace of copper is dissolved, but we feel justified in not calling it a complex salt.

II. VALENCY OF PROTEIN NITROGEN

(The Basis for Configurations)

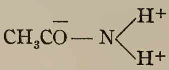
The chemistry of protein has to some extent resolved itself into the chemistry of nitrogen. It is clear from a review of these salts that certain conditions of nitrogen are associated with certain marked and characteristic colors. For example, a dipeptide copper salt, containing two nitrogen atoms, gives in an alkaline solution a color similar to that of an ammonia complex; a tripeptide, containing three nitrogen atoms, gives a deep bluish violet color; while a tetrapeptide, with four nitrogen atoms, gives a red phenolphthalein color, indicating the additive influence of a nitrogen group on the complex.

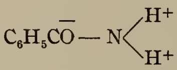
A brief review of the valency[1] of nitrogen in the ammonia group is not out of place here, as it is the only basis for these configurations that we can propose. In ammonia we have three positive hydrogen atoms, or three positive valences. In ammonium compounds, such as ammonium chloride, the nitrogen has at least four valences and perhaps five. In other words, nitrogen is capable of combining, directly or indirectly, with five monovalent elements, and not more. If one is negative—and there must always be one negative element to a pentavalent nitrogen—and the other four positive, the group is quite stable. A nitrogen compound containing two negative and three positive elements is unstable, but capable of existence in equilibrium with an excess of one of the negative elements.[2]



Trimethylamine Dibromide

The amides also, such as acetamide, benzamide, etc., belong to this class:





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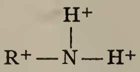
[1] Taken mostly from H. Kauffmann's "Die Valenzlehre," and from Werner's "New Ideas in Inorganic Chemistry."

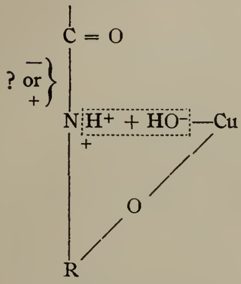
[2] Remsen: THIS JOURNAL, **18**, 91. Hantzsch and Graef: Ber. d. chem. Ges., **38**, 2154 (1905).

and form unstable hydrochlorides. Here also there would be two negative and three positive valences. Therefore in the amino acids we must consider the nitrogen as having practically three positive valences:

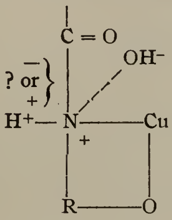


$$R^{+}-\overset{\overset{\displaystyle H^{+}}{|}}{N}-H^{+}$$

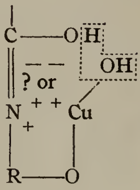
Keeping all these facts in mind, we can conceive of the imino group combining with the copper in three ways:



I. Trivalent Nitrogen

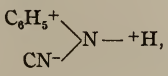


II. Pentavalent Nitrogen



III. Trivalent Nitrogen

So far we have found no reason for believing that the hydrogen of the imino group of a peptide can be replaced by copper. If the nitrogen has one negative group or valence (Reaction I), as in phenylcyanoamide,[1]



$$\begin{matrix} C_6H_5^{+} \searrow \\ N - {}^{+}H, \\ CN^{-} \nearrow \end{matrix}$$

the hydrogen becomes replaceable.

If nitrogen has two negative groups, as in

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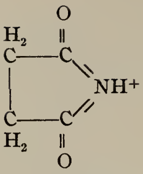
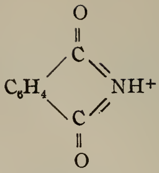
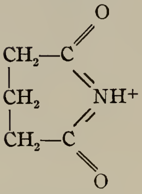
[1] From H. Kauffman: Die Valenzlehre, p. 351.



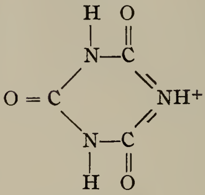
Succinimide[1]



Phthalimide[2]



Glutarimide[3]

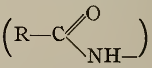
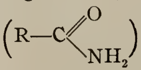


Cyanuric Acid[4]

the hydrogen atom also becomes replaceable.

On the other hand, biuret[5] and the other amides whose nitrogens have two positive and one negative valences seem not to have a replaceable hydrogen atom.

Hantzsch[6] and E. Voegelen have shown that the amides $R.CONH_2$ are quite neutral nonelectrolytes, which do not, to any appreciable extent, form salts in aqueous solution with alkalies or acids.

Therefore if we can expect the imino groups  $\left(R—C\begin{matrix}\nearrow O \\ \searrow NH—\end{matrix}\right)$ to have a replaceable hydrogen atom, we should certainly expect it in an amide group  $\left(R—C\begin{matrix}\nearrow O \\ \searrow NH_2\end{matrix}\right)$ where two hydrogen atoms are available. As Van Slyke[7] has shown with asparagine, and as we have determined with the following amides and imino derivatives, the amide nitrogen does not liberate free nitrogen with nitrous acid, and thus in this respect also resembles the imino group.

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[1] Landsberg: Ann. Chem. (Liebig), **215**, 200.

[2] *Ibid.*

[3] Bodtker: Dissertation.

[4] Beilstein: Handb. org. Chem., **I**, 1267.

[5] Schiff: Ber. d. chem. Ges., **29**, 299 (1896).

[6] *Ibid.*, **34**, 3143 (1901).

[7] J. Biol. Chem., **9**, 185 (1911).

Amides and Imino Substances

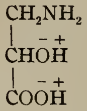
Amino-nitrogen determinations, using Van Slyke's method[1]

Substance	Weight of sample	Cc. nitrogen evolved, standard conditions		Cc. nitrogen on blank tests (ave.), standard conditions		Cc. nitrogen corrected for controls		Per cent. amino nitrogen	Per cent. total nitrogen
Amides	Grams	10 min.	20 min.	10 min.	20 min.	10 min.	20 min.		
Acetamide	0.1161	1.47	1.84	0.65	0.73	0.82	1.11	0.61	23
Chloroacetylasparagine	0.2011	0.64	0.77	0.65	0.73	....	0.04	0.01	13
Bromopropionylasparagine	0.1029	0.87	0.91	0.65	0.73	0.22	0.18	0.10	10
Bromocaproylasparagine	0.1047	0.72	0.76	0.65	0.73	0.07	0.03	0.01	9
Benzoylasparagine	0.1061	0.91	1.00	0.65	0.73	0.26	0.27	0.15	16
Biuret	0.1070	1.25	1.61	0.65	0.73	0.60	0.88	0.51	40
Imino derivatives									
Formyl-*d*-leucine	0.1001	0.62	0.71	0.65	0.73	....	....	....	8
Benzoylleucine	0.1031	0.62	0.67	0.65	0.73	....	....	....	5
Hippuric acid	0.1013	0.64	0.73	0.65	0.73	....	....	....	7
Cyanuric acid	0.1048	0.73	0.86	0.65	0.73	0.08	0.13	0.07	32

[1] These determinations were made by Mr. E. N. Rosenfeld, in this laboratory.

But if we consider that the imino group in peptides has only positive valences, the presence of replaceable hydrogen would be exceptional and unexpected. If we consider the imino derivatives as having one negative group (and this would favor or permit of one hydrogen atom being replaceable), then a bromo or chloro derivative of a di-, tri-, or tetrapeptide ought to give a considerable quantity of dibasic salt. This it does not do. One amino substance, containing only one nitrogen atom, and acting toward copper as a dibasic substance, should be considered in this discussion:

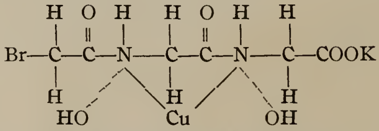
Isoserine or β-amino-α-hydroxypropionic acid,



$$\begin{array}{l} \mathrm{CH_2NH_2} \\ | \\ \mathrm{CH\overset{-}{O}\overset{+}{H}} \\ | \\ \mathrm{CO\overset{-}{O}\overset{+}{H}} \end{array}$$

The question here too is, is it the hydrogen of the NH_2 group or of the hydroxy group that is replaceable? We believe with Fischer that the hydrogen of the hydroxy group acts as an acid ion, and that the NH_2 group does not participate in the neutralization of the second OH group of the copper. If it did participate, the nitrogen group would be negative, and therefore would not show the usual blue color characteristic of a complex. The color, however, does not seem to differ from that of most amino acid copper complexes.

We are therefore forced to the conclusion that the *second principal valence of copper combines only with the partially basic nitrogen of the imino group* (Reaction II), and in substances like chloro and bromo acid derivatives of amino acids the nitrogen is no longer basic, and therefore is incapable of forming complexes. The same is true of similar derivatives of dipeptides in neutral solution, but in excess of alkali[1] these substances are at least partially basic.



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[1] It might be suggested that the excess of alkali replaces the Br with a OH group, but qualitative tests have not shown any appreciable hydration.

This means that a complex is formed in these derivatives only when in the presence of an excess of negative ions, because of the fact that the bromine atom gives a higher negative charge to the third valence of the nitrogen, and in this respect the compound is similar to trimethylamine dibromide.

The exact position of the second OH ion from the copper remains to be determined. According to Werner, if the reaction II occurs, the OH group is ionizable, and should therefore give an alkaline solution. This we have not found, yet our failure to find any alkalinity may be due to the fact that there are two or more nitrogen atoms that are capable of combining with this OH group, thereby reducing its concentration in solution to an inappreciable amount. We hope to say more on this subject later.

III. BIURET REACTION FOR PROTEINS

As we mentioned in the first paper, the biuret reaction is considered the most reliable of the protein tests. Speaking chemically, what does this reaction mean, what configuration does it involve? By *biuret color* is generally meant a violet or red color, obtained with a small amount of copper salt and a good excess of alkali. Often a color is called *biuret* when it is mixed with a considerable amount of ordinary copper-complex blue, and considerable confusion has arisen from this misuse of terms. On the basis of the preceding data we wish to propose the following theory in reference to the biuret reaction, and to show the direction along which our experiments have led us.

For the present we shall use the following terms: (*a*) *Biuret color;* a purple-red, resembling somewhat an alkaline phenolphthalein solution in color. Colors having a bluer tint we shall term (*b*) *partial biuret*, or *semibiuret*, as some are probably mixtures of pure *biuret* and ordinary complex-blue. Another term we should like to fix: (*c*) *Biuret reaction* of a peptide; the color reaction obtained on adding a large excess of alkali to the peptide when it is *completely combined* with copper, i. e., the color reaction of its *alkaline copper salt.*

If we classify the peptides according to these terms we find that:

I. All *simple dipeptides* made from monoamino acids, excluding their amide derivatives, give about the same color with copper in alkaline solution—a deep blue color like that of the ammonia-copper complex.

II. The neutral copper salts of all *tripeptides*, made from monoamino acids, excluding their amide derivatives, and of all *amides of dipeptides* change color on the addition of excess of alkali. They give shades of the "semibiuret" color, the shade varying with the constituent amino acids and the temperature.[1]

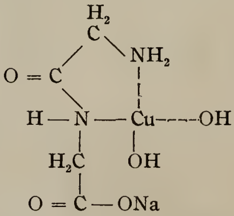
III. The color of the neutral copper salts of all *tetrapeptides* of monoamino acids, and of *amides of tripeptides*, changes on addition of excess of alkali from the deep blue of their neutral copper complex to the purple-red "biuret color."

To summarize:

I. When a substance is so combined with copper that *only two nitrogen atoms* are connected with the copper in a ring formation,[2] stable in excess of alkali, the result is a *deep blue color*, resembling that of the copper-ammonia complex.

For example:

(*a*) All simple dipeptides made from monoamino acids, like



Alkaline Copper Glycylglycine

(*b*) All carboxyl derivatives of simple dipeptides made from monoamino acids; such as

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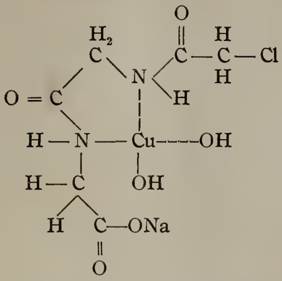
[1] The amount of biuret color seems to increase with rise in temperature, which fact would suggest that an equilibrium exists between the blue and red substances.

[2] By "ring formation" we mean formations of not more than six members.

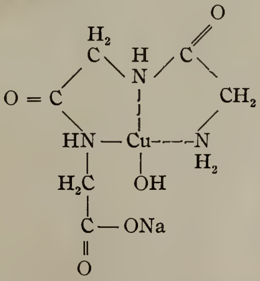


Alkaline Copper Chloroacetylglycylglycine

II. When *three nitrogen atoms* are connected with copper in a ring formation that is stable in excess of alkali, a "*semi-biuret*" *color* is produced.

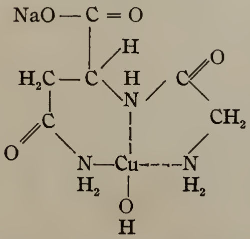
For example:

(*a*) All simple tripeptides made from monoamino acids, such as



Alkaline Copper Glycylglycylglycine

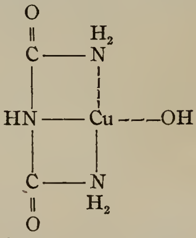
(*b*) All amides of simple dipeptides made from monoamino acids, such as



Alkaline Copper Glycylasparagine

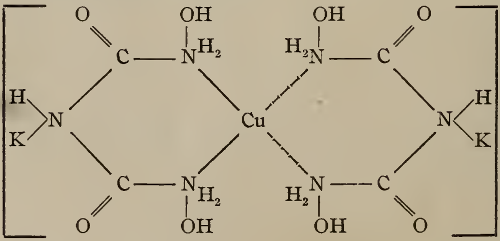
(*c*) Various diamides, and other substances studied by Schiff. Some of these, when fully combined with copper, will probably give a blue complex color, and they probably have only two nitrogen atoms connected in the ring with the copper atom and belong to the first class of salts. (Owing to our lack of quantitative data on the subject, however, we suggest only one configuration, that of biuret.) Furthermore, when the amount of substance is in large excess, as is usually the case when the biuret test is made, two or more molecules of the substance may combine to form a mixture of nitrogen complexes. Thus:

A "semibiuret" complex (see experimental notes, page 410)



(Four-membered rings)

and a "true biuret" complex:[1]



III. When *four nitrogen atoms*, as in the case of biuret copper just shown, are connected with the copper in a ring formation that is stable in excess of alkali, a *purple-red color* resembling that of phenolphthalein in alkaline solution is produced. *This is the true biuret color.*

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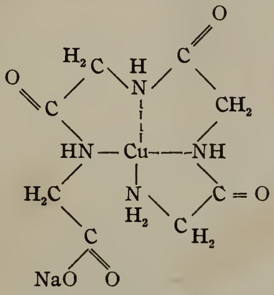
[1] Schiff's compound with our idea of structure, which fits his analyses. Ber. d. chem. Ges., **29**, 298 (1896). (See discussion, page 394).

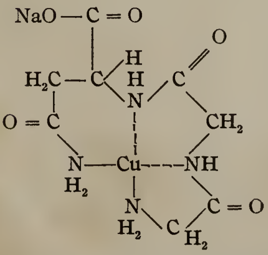
Examples:

(*a*) All simple tetrapeptides made from monoamino acids, as



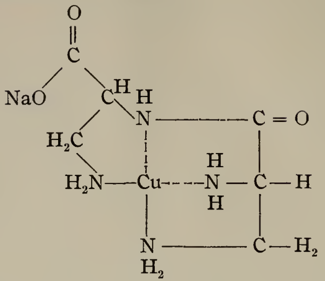
Alkaline Copper Triglycylglycine

(*b*) All amides of simple tripeptides made from monoamino acids, as



Alkaline Copper Diglycylasparagine

(*c*) Some diamino acid dipeptides, as



Alkaline Copper Diaminopropionic Acid Dipeptide

Fischer[1] found that this substance was the only dipeptide giving a strong biuret reaction, and was inclined to doubt the identity and purity of the substance. If our supposition is correct, there can be no question as to the identity of this substance, as our results support Fischer's work. But our work has not yet made clear which of the two possible isomers it is that produces the biuret configuration.

IV. A REVIEW OF PREVIOUS WORK ON ALLIED COMPOUNDS

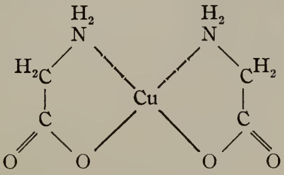
So far we have given the results of our own investigations and those of Fischer and Abderhalden, and have given a chemical structure of the "biuret configuration." There was *much pioneer work* done by Schiff, Tschugaeff, Ley and Werner, and we append here a discussion, necessarily brief, of their work in reference to ours.

Schiff,[2] who studied very many substances containing $CONH_2$ and NH groups, for the most part qualitatively, in order to find a structural basis for the biuret reaction, came to the following conclusion: "Als Biuretreaction sollte man systematisch nur diejenige bezeichnen welche durch Kupfer- oder Nickelsalze mit Aminoamiden oder Diamiden erhalten wird, welche schliesslich auf die drei Grundformen: Biuret, Oxamid und Malonamid und ihre Substititionproducte zurückgeführt werden können."

[1] Fischer: Untersuchungen über Aminosäuren, Polypeptide und Proteine, p. 50.
[2] Schiff: Ann. Chem. (Liebig), **299**, 240; **352**, 73–87.

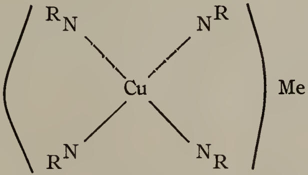
Some of the colors Schiff called biuret belong in all three of our classes; and until the amount of copper is determined in connection with the character of the color, very little can be said of possible configurations. We have every reason to believe that when this is done the results will, as we have indicated with biuret itself, be in accord with the biuret configuration given above.

Ley[1] believes that the copper complexes of amino acids are ring formations, as in

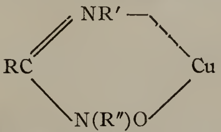


Copper Glycine

and that the abnormal color is due to the action of secondary valences. When both secondary and principal valences are connected with the copper, a red or violet-red color results, and the substance has, according to Ley, the following configuration:



These ideas are fully supported by our work on the peptides, but we are not ready to accept his structure of the copper salt of 1-phenyl-3-benzylhydroxyformamidine, which he gives as



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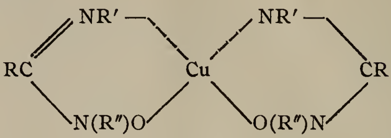
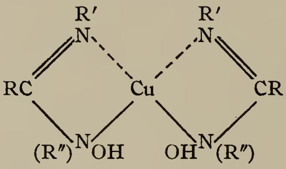
[1] Ley: Z. Electrochem., **1904**, 954; **1905**, 585. Ber. d. chem. Ges., **40**, 705; **42**, 366.

The analysis of this red copper salt is consistent with the formula $(C_{14}H_{13}ON_2)_2Cu$, and according to Ley the formula should be written

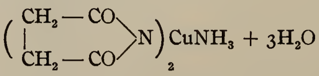


The fact that the salt is red leads us to doubt that its structure should be such. If our ideas, as stated in connection with the peptides, are correct, this salt has the following structure:

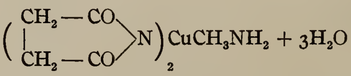


This conception is more consistent with the very weak acid properties of the hydroxyformamidine.

Tschugaeff[1] found that succinimide combined with copper hydroxide and amines to form crystalline salts. Those with three nitrogen atoms attached to the copper (two succinimides and one amine) gave crystals of a deep blue-violet to violet color. They are as follows:



$$\left(\begin{array}{l}CH_2-CO\diagdown\\ |\qquad\qquad\quad >N\\ CH_2-CO\diagup\end{array}\right)_2 CuNH_3 + 3H_2O$$



$$\left(\begin{array}{l}CH_2-CO\diagdown\\ |\qquad\qquad\quad >N\\ CH_2-CO\diagup\end{array}\right)_2 CuCH_3NH_2 + 3H_2O$$

These salts on dissolving in water yield a deep blue color, no doubt the results of hydrolysis; the imide nitrogen, being negative, dissociates in aqueous solution, as in the case of ordinary copper salts. *The bluish violet color* of the *crystals*, and *the three nitrogen atoms* attached to the copper, would cause these salts to be *included in our second class*, the class *giving a "semibiuret" color.* Those with four nitrogen atoms connected with the copper atom, two being of the imide and two of the amines, yield brown-red or "copper-red" crystals. They are as follows (Su = succinimide):

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[1] Tschugaeff: Ber. d. chem. Ges., **37,** 1480; **38,** 2904; **40,** 1977.

$(Su)_2Cu.2(NH_3)$
$(Su)_2Cu.2(CH_3NH_2)$
$(Su)_2Cu.2(C_2H_5NH_2)$
$(Su)_2Cu.2(C_3H_7NH_2)$
$(Su)_2Cu.2(C_4H_9NH_2)$ (normal)
$(Su)_2Cu.2(C_4H_9NH_2)$ (iso)
$(Su)_2Cu.2(C_4H_9NH_2)$ (sec.)
$(Su)_2Cu.2(C_9H_4NH_2)$ (tert.)
$(Su)_2Cu.2(C_5H_{11}NH_2)$ (iso)
$(Su)_2Cu.2(C_6H_{13}NH_2)$ (normal)
$(Su)_2Cu.2(C_3H_5NH_2)$
$(Su)_2Cu.2(C_9H_{15}CH_2NH_2)$[1]
$(Su)_2Cu.2(CH_3)_2NH$
$(Su)_2Cu.2(C_5H_5N)$[2]

Tschugaeff found the following salts, which also have a red color (Ph = phthalimide, Gl = glutarimide):

$(Ph)_2Cu.2(NH_3)$
$(Gl)_2Cu.2(C_6H_5CH_2NH_2)$

These red salts, on dissolving in water, give also a deep blue color, due no doubt to hydrolysis. Tschugaeff finds that the following tetraimide copper salts also yield the biuret color:

$K_2Cu(Su)_4.6H_2O$, light red-violet
$Rb_2Cu(Su)_4.2H_2O$, red-violet
$CsCu(Su)_4.2H_2O$, red-violet

but his sodium and lithium compounds unexpectedly gave only a blue color:

$Na_2Cu(Su)_4.5H_2O$, blue
$Li_2Cu(Su)_4.H_2O$, blue

The reddish color of most of these salts, and the presence of *four nitrogen atoms connected to the copper*, cause these salts to be *included in our third class of substances giving a "true biuret" color.* From our experience this decided difference between the sodium and potassium salts seems most improbable; and we think it likely that the former is a molecular substance, while those having the red color are atomic complexes.

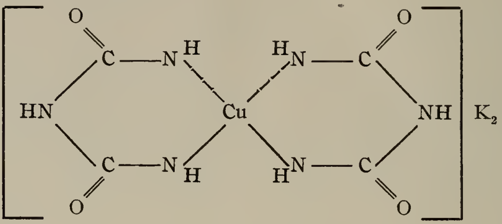
---

[1] Camphylamine compound.

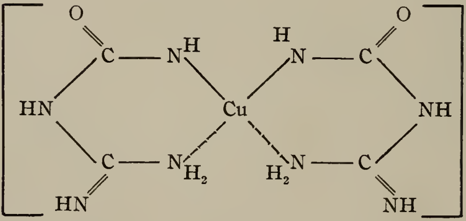
[2] Pyridine compound.

That Tschugaeff came to practically the same conclusion in regard to the "biuret configuration" can be seen from his structure of red copper salts of biuret (I), dicyanodiamidine (II), and diguanidine (III):

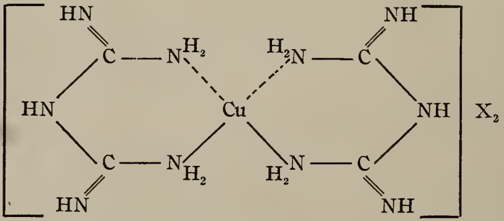
(I)



(II)



(III)



These configurations are, we believe, very nearly correct, but we cannot come to the same conclusion as regards some of the details. As may be seen in (I), each of the four amides has lost one hydrogen atom, which Tschugaeff believes are removed by neutralization. Schiff's[1] analyses do not support this idea, and we have shown on page 393 our reasons for not accepting it. The same may be said of Formula (II). Owing to lack of analytical data we defer discussing other minor points.

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[1] Schiff: Ber. d. chem. Ges., **29**, 298.

V. GENERAL DISCUSSION AND CONCLUSIONS

On reviewing all the complexes, we find that about *25 substances* containing *one copper* and *four nitrogen atoms* in the molecule *give a "red biuret" color*; that about *30 substances* containing *one copper* and *three nitrogen atoms* give a *"semibiuret" color*; and that about *25 substances*, containing *one copper* and *two nitrogen atoms* give a *deep blue color*. Slight variations in color in occasional substances may be due to the influence of the various groups or radicals, as well as to variations in temperature. We intend to study this phase of the question spectrographically in the near future.

That the amide, imide, imino and amino substances combine coördinately (in the sense used by Werner), there is little doubt, but several points remain to be cleared up, i. e., the exact fate of the second OH group of the copper. According to Werner, it ought to be ionizable, and therefore render the solution alkaline. That most of these peptides are stable in excess of alkali is in favor of that hypothesis.

Summary

We have found that:

I. All *simple dipeptides* made from monoamino acids (excluding their amide derivatives), and *their carboxyl derivatives*, give about the same color with copper in alkaline solution—a *deep blue color* like that of the ammonia-copper complex.

II. The neutral copper salts of all *tripeptides*, made from monoamino acids, and *their carboxyl derivatives* (excluding their amide derivatives), and of all *amides of dipeptides* change color on the addition of excess of alkali. They give shades of the *"semibiuret" color*, the shades varying with the constituent amino acids and the temperature.

III. The color of the neutral copper salts of all *tetrapep-*

tides of monoamino acids, and of *amides* of *tripeptides*, change on addition of excess of alkali from the deep blue of their neutral copper complex to the *purple-red "biuret color*."

IV. Our experiments seem to show that a *true biuret* reaction can occur only when *four nitrogen atoms* are so arranged that they can *combine "coördinately" with the copper* in an *alkaline solution*.

V. A *semibiuret reaction* can occur only when *three nitrogen atoms* are so arranged that they can combine "*coördinately*" with the *copper* in *an alkaline solution*.

VI. EXPERIMENTAL

Molecular Weight Determinations by the Freezing Point Method

The determination of the molecular weights of copper salts involves several considerations:

(1) Purity of the copper salt. The only method of purification that would insure the purity of these substances is recrystallization. With the exception of a few peptides, this method is very difficult to follow, as most copper salts do not crystallize readily. A few salts, however, such as leucylglycine and leucylleucine, crystallize easily.

(2) Concentration of solute. The copper salts of dipeptides referred to above dissolve only to a slight extent, and their insolubility does not permit of many variations in the concentration of the solute.

The results show that in leucylglycine copper the amount of free OH ion is quite small, whereas in glycylglycine copper it may be quite appreciable. They also show clearly enough that two molecules of copper complexes are not combined into one molecule in aqueous solutions.

Substance	W	K	L	Δ	M (found)	M (calculated)
Glycine	0.1969	1850	24.39	0.199	75.0	75.07
Glycine	0.2005	1850	23.88	0.208	74.7	75.07
Copper glycylglycine(OH)	0.1969	1850	25.12	0.099	146.0	211.7
Copper glycylglycine(OH)	0.1952	1850	24.54	0.090	164.0	211.7
Copper glycylphenylglycine(OH)	0.1001	1850	24.07	0.028	281.0	323.6
Copper leucylglycine(OH) H_2O	0.1960	1850	28.87	0.031	405.0	285.8
Copper leucylglycine(OH) H_2O	0.0982	1850	24.54	0.021	353.0	285.8
Copper leucylglycine(OH) H_2O	0.1451	1850	24.42	0.035	316.0	285.8
Copper leucylglycine(OH) H_2O	0.2017	1850	24.75	0.052	290.0	285.8
Copper leucylglycine(OH) H_2O	0.2003	1850	24.79	0.062	241.0	285.8
Copper leucylglycine(OH) H_2O	0.2043	1850	23.72	0.055	290.0	285.8
Copper leucylglycine(OH) H_2O	0.2931	1850	23.65	0.077	298.0	285.8

$$M = \frac{KW}{\Delta L}$$

M = molecular weight.
W = weight of substance dissolved.
K = constant of solvent, water.
L = weight of solvent, water.
Δ = depression of freezing point.

Biuret

We made biuret copper in two ways:

First, about 0.1000 gram of biuret was dissolved in 20 cc. normal sodium hydroxide. While constantly stirring in ice mixture, cold copper hydroxide was added little by little until the red color of biuret changed slightly toward a blue. The biuret copper was then dissolved with acetic acid and titrated as usual.

The theoretical amount of copper oxide, according to Schiff's work, should be one molecule for every two of biuret. As the following tables show (Specimens A), practically this result was obtained.

Second, about 0.1000 gram of biuret was dissolved in different amounts of normal sodium hydroxide—30, 40 and 50 cc.—cooled in ice and mixed with *an excess of cold copper hydroxide.* After stirring for 5 or 10 minutes and filtering through a Gooch crucible,[1] the amount of copper was determined by titration with the usual technic. The results in the following table (Specimens B) are consistent with the formula $(\text{Biuret})_1\text{Cu}_1$:

	Substance	Weight of sample Gram	CO_2 free N NaOH used Cc.	CuO in[4] filtrate Gram	Theoretical wt. of CuO calc. for this sample Gram	Per cent. CuO in alkaline filtrate to theory
A	Biuret	0.1011	20	0.0355	0.0387[2]	91.5
A	Biuret	0.1024	20	0.0371	0.0391[2]	94.9
B	Biuret	0.1004	30	0.0696	0.0768[3]	90.1
B	Biuret	0.1008	40	0.0744	0.0772[3]	96.4
B	Biuret	0.1010	50	0.0747	0.0773[3]	96.6_4

Calorimetric Measurements on the Heat of Formation of Copper Salts

Since each of these copper salts contains one atom of copper, it is natural to expect that if their formation is dependent on the neutralization of copper hydroxide, the heat of formation will in each case be the same. We have not attempted accurate experiments on this question, as they would require the use of too much expensive material. The following table, therefore, gives only a qualitative demonstration of the relative amounts of heat given off in the formation of copper acetate, copper glycine and copper glycylglycine when only 0.01 mole is formed.

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[1] Filter paper cannot be used with biuret copper. Therefore a Gooch crucible with an asbestos mat was employed.

[2] For two molecules of biuret to one of copper.

[3] For one molecule of biuret to one of copper.

[4] Blank tests on the reagents were made and corrections applied.

The experiments were carried out in a Dewar flask, which served very well as a calorimeter.

Substance	Molecular weight	Weight of 0.01 mole Grams	Gross calories per 0.01 mole of salt
Copper hydroxide	97.6	0.976	..
Acetic acid	60.0	0.600	44
Glycine	75.07	0.7507	26
Glycylglycine	132.14	1.3214	13

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A STUDY OF THE CONDUCTIVITY AND DISSOCIATION OF CERTAIN ORGANIC ACIDS IN AQUEOUS SOLUTION AT DIFFERENT TEMPERATURES

By A. Springer, Jr., and Harry C. Jones

INTRODUCTION

A careful review of the work previously done on the conductivity and dissociation of organic acids in aqueous solution has already been made by White and Jones[1] and by Wightman and Jones;[2] so that any historical sketch that we might give would be superfluous. We shall therefore proceed at once to the experimental part of our work, and, in the discussion which follows, reference will be made to all important articles having direct bearing on our results.

This particular investigation has been in progress for somewhat more than two years. During the first year, conductivity measurements were made at temperatures between zero and thirty-five degrees. During the second year the conductivities of the same acids—as well as some already used by White and Jones at lower temperatures—were taken at temperatures ranging from thirty-five to sixty-five degrees. The two sets of results at thirty-five degrees were compared, and by this method we had a means of comparing the work of the two different years. Some of these agreements and disagreements will be tabulated in another place. The two sets of measurements, for any given acid, were made with different apparatus, different solutions, usually with different specimens of the acid, and frequently by different investigators.

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[1] This Journal, **44**, 159 (1910).

[2] *Ibid.*, **46**, 56 (1911).

Reagents

The water used in all this work was prepared in the manner always employed in this laboratory and adequately described by Jones and Mackay.[1]

The acids used were obtained in most cases from Kahlbaum. They were, with one exception, purified by filtration and recrystallization from conductivity water. Before weighing, they were always carefully dried over sulphuric acid in a vacuum desiccator. Their melting points were taken, whenever possible, as a test of their purity. The most concentrated solution used was made up by direct weighing and standardized by titration against a solution of sodium hydroxide of known concentration. The only acid that we could not treat in this manner was dichloroacetic. This we did not purify at all, it being the best obtainable (distilled from chloral). Being a liquid at ordinary temperatures and hygroscopic, it could not be weighed accurately. The mother solution was, therefore, prepared by the usual titration method.

Apparatus

The conductivity cells were of the type used by Jones and Bingham.[2] Briefly, these have platinum electrodes (coated with platinum black) attached to glass tubes containing mercury, the tubes being sealed into ground-glass stoppers. A special cylindrical type of cell[3] was used for determining the conductivity of the water.

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[1] THIS JOURNAL, **19**, 91; Z. physik. Chem., **22**, 237 (1897).

[2] THIS JOURNAL, **34**, 493 (1905).

[3] *Ibid.*, **45**, 282 (1911).

The cell constants were taken in the manner described by White and Jones. During the low temperature work the cells were standardized about once a month. While working at elevated temperatures this was done even more frequently.

When this investigation was begun, an ordinary Wheatstone bridge was employed. Soon, however, we secured from Leeds and Northrup a very fine Kohlrausch slide-wire bridge, by means of which it was possible to read to fractions of a millimeter.

The resistance box, thermometers, thermostats, and other apparatus scarcely require detailed description. In general, all the precautions were taken which Wightman and Jones recommend.

Procedure

The method of procedure for measurements at the lower temperatures has already been described in several papers from this laboratory.

But at the more elevated temperatures much less has been done. Wightman and Jones[1] have been working simultaneously with us on this problem, and their work has just been published. Clover and Jones[2] and West and Jones[3] are our only predecessors. A brief review of their work might not be out of place here.

Clover and Jones encountered a number of difficulties, in their higher temperature measurements, which had never been noticed in the lower temperature work. The cell constants changed frequently. The solubility of the glass was noticeable. The coefficient of expansion of water had to be taken into consideration. How they coped with these problems will be seen from the following quotations, taken from their paper: *Cell constants.* "It has developed that a strain is brought about by the high temperatures, which may result in a change either in the distance of the electrode plates from each other or in the surface of the plates.

"Since such a variation had not previously been observed in work covering a range from 0° to 35°, it was thought that the changes might be reduced by maintaining the cells at a temperature which was about a mean of those employed in the experimental work. Accordingly, when not in use, the cells were filled with pure water and placed in a bath which was maintained continuously at a temperature of 45° to 50°."

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[1] This Journal, **48**, 320 (1912).

[2] *Ibid.*, **43**, 187 (1910).

[3] *Ibid.*, **44**, 508 (1911).

They then describe the following experiment:

"The measurements were first carefully made at 35° and duplicated; then the regular systematic procedure was gone through at 65°, and after this the readings at 35° were again made. If the results obtained the second time should agree with those first obtained at 35°, this would be strong evidence that the method was reliable. It was found in some cases that the second reading differed slightly from the first. In other cases there was no difference, and the change appeared to be independent of the cell used, or the concentration of the solution. It was found, further, that on standing for a considerable length of time at 35° (2 or 3 hours) *the reading slowly changed back in all cases to the original value.* It is difficult to see what other cause can be assigned to these results than a temporary change in the cell constant during the heating at 65°."

Solubility of Glass.—"In conductivity work at ordinary temperatures this factor has always been neglected, and probably is not sufficiently large to influence the results even with very dilute solutions. However, at 50° the error introduced by this factor at a dilution of 1000 is greater than any of the other ordinary experimental errors. At 65° the solubility of the glass is still greater, and at 80° the conductivity of pure water is increased tenfold on remaining in the cell for a couple of hours. In this connection it may be stated that the cells employed were made of hard glass. Of course, the amount of glass dissolved depends upon the exact nature of the latter, and was found to vary considerably with the different cells used, and at different intervals in the case of any one cell. The idea of introducing a correction for the solubility of the glass was abandoned, but the difficulty was overcome in another way. It was found that after the cells had been heated with water for several hours the amount of glass dissolved gradually decreased and finally amounted to practically nothing. After this treatment, as the cells were kept in a bath at 45° and 50° and the water in them changed once a day, the solubility of the glass at 65° was always practically nothing, or entirely negligible. If a cell were removed from the bath and allowed to stand filled with water at room temperature for any length of time, it was found that glass was again dissolved on heating."

Because of the great increase in the coefficient of expansion of water with rising temperature, Clover and Jones found it necessary to make up the solutions at the *exact temperature* at which they were to be measured. That is, for the same acid, one set of solutions was prepared at 50° and another at 65°. The solutions prepared at the former temperature were also used for measurements at 35°, and the correction factor 0.994 was then applied.

It was found advisable nearly to fill the cells with the solution for the following reasons: "First, to minimize any slight change in concentration brought about by condensation or escape of the solvent, or from any other cause. Second, to exclude the air with its accompanying carbon dioxide from the cell, as the oxide would be dissolved during the manipulation and would influence the results with dilute solutions. Third, to prevent difficulty in opening the cells. With a large air space diminished pressure is quickly produced on removal from the bath, and if the cells can be opened at all it can be done only at the risk of distorting the electrodes."

In the following year West and Jones took up again the problem of conductivity measurements at relatively high temperatures. They found that by heating the glass vessels first with dilute sodium hydroxide, then with dilute hydrochloric acid and lastly with conductivity water, the solubility of the glass could be reduced to a negligible quantity.

They also devised the following method for determining the cell constants: "The standard solution of potassium chloride was placed in the cell. The cell was then heated to 50°, and after remaining at that temperature for about an hour was cooled to 20°. *As soon as temperature equilibrium* was established at 20° the conductivity readings were made and the cell constants calculated." In this manner the constants of the cells, with electrodes and everything in the 50° bath, were taken at 20°, where the conductivity of the standard potassium chloride is known. Clover and Jones had previously found (as stated above) that the cells would be required to stand in a 20° bath for *several hours* before their electrodes would resume the 20° position.

Probably the most beneficial contribution that West and Jones made to this work was their method for preparing solutions. The following brief quotation explains both the method and its advantages:

"Since we worked over a range of temperature of only 30°, we found it convenient to prepare the solutions at the intermediate temperature, 50°, and then to use the solutions at the three temperatures, 35°, 50° and 65°. But since the volume of a solution varies with the temperature it was, of course, necessary to apply a correction at 35° and 65° to the volume of solutions made up at 50°.

"When a standard solution is cooled from 50° to 35° there is a contraction in volume and a subsequent increase in the concentration of the solution. The value of μ_v for any solution would, therefore, be slightly too large. The value of μ_v as found must be multiplied by the factor 0.994 for results at 35° when the solutions were made up at 50°. The correction factor for solutions made up at 50° and used at 65° is 1.0076.

"The coefficient of expansion for distilled water is somewhat less than that for an aqueous solution. However, the difference in the coefficients for water and for that of our most concentrated solution is so small that it is negligible.

"By making use of the above correction it was necessary to prepare only one set of solutions for each salt; and, consequently, much pure material and time were saved."

When we began the investigations at higher temperature these two questions presented themselves:

First. If the cells give evidence of soluble glass whenever they are heated to 50°, cooled to room temperature and then heated to 50° again, will not the measuring flasks show this same tendency? For the measuring flasks are not kept in the heated bath, when not in use.

Second. When a solution at 50° is poured into a burette, then transferred to a measuring flask slowly, so that the burette may drain, what will be its temperature at the end of the procedure? Clearly not 50°, since a burette has a large surface in contact with the cool air of the room. And the process of draining at best must require two minutes or more. So when the experimenter imagines he is drawing off x cc. at 50°, he is actually drawing off x cc. at some lower temperature—that is, more than x cc. at 50°.

A simple device did away with both these possible sources of error. At 50°, 988.07 grams of distilled water have a volume of 1000 cc. Our liter flask was weighed at 20°. Then 988.07 grams of distilled water at 20° were introduced—air displacement being taken into account. The flask was marked at the bottom of the meniscus. This flask filled to the mark with water at 20° (room temperature) will contain a liter at 50°. Therefore, all the mother solutions could be made up for 50° work at 20°, and the solubility of the glass, which is noticeable only at higher temperatures, is thus made negligible.

This mother solution will be, let us say, normal at 50°. At 20° it is stronger than normal. If we draw out 100 cc. at 20° and dilute it to a volume of 200 cc. at 20° it will also be stronger than half normal. But heat this latter solution to 50° and it will again attain its required normality—assuming that the coefficient of expansion of water is the same as that of dilute solutions. And all solutions worked with were eighth-normal, or more dilute. This permits us to titrate all solutions at room temperature, which obviates the second of the above difficulties.

The values of the limiting conductivities (μ_∞) of the monobasic organic acids were calculated from the μ_∞ of their sodium salts. This well known method consists merely in deducting the migration velocity of the sodium ion from the value of the sodium salt, and in substituting in its place the migration velocity of the hydrogen ion. The equation of White and Jones[1] is self-explanatory.

μ_∞ (acid) = μ_∞ (Na salt of acid)—μ_∞ (NaCl) + μ_∞ (HCl). The μ_∞ values for hydrochloric acid and sodium chloride have been determined by previous workers. The sodium salt of the acid in question was made by titration of the acid with sodium hydroxide from alcohol—phenolphthalein being used as an indicator. Only solutions of a concentration of N/2048 were used, since it was found by White and Jones[2] that the μ_∞ values of the sodium salts generally occur at this concentration.

For dibasic organic acids the μ_∞ of the sodium salt cannot be directly determined. Ostwald[3] has, however, described a satisfactory method for obtaining the value of μ_∞ for the acid. Dibasic acids, he says, in most cases dissociate like monobasic acids—setting free only one hydrogen cation. And the limiting conductivities of monobasic acids seem to be a function of the number of atoms contained in the anions. Therefore, a dibasic acid having 16 atoms should give the same μ_∞ value as a monobasic acid containing 16 atoms; and the latter value can be experimentally obtained.

The following table shows the limiting conductivities of all the acids with which we worked. These acids are arranged in the order of the number of atoms contained in their molecule. The values for the dibasic acids were worked out as described above.

The four asterisked values—pyromucic acid at 0° and 25° and sulphanilic and metanilic acids at 0°—are taken from the data of White and Jones.[4] At 35° their values coincide exactly with ours.

Dibromosuccinic and sulphosalicylic acids are omitted from the following list. As may be seen from their conductivities, they do not dissociate as monobasic acids; therefore, the method of Ostwald for finding their μ_∞ could not be employed.

[1] THIS JOURNAL, **44**, 159 (1910).

[2] *Ibid*, **44**, 161 (1910).

[3] Z. physik. Chem., **1**, 74 (1887).

[4] THIS JOURNAL, **44**, 163 (1910).

Acid	Atoms	*Limiting Conductivities* 0°	15°	25°	35°	50°	65°
Dichloroacetic	8	221.7	305.6	359.3	408.7	477.3	545.8
Bromosuccinic	10	222.2	302.1	354.1	...	...	...
Pyromucic	12	223.0*	...	355.0*	405.0	471.0	539.2
Salicylic	16	...	...	...	403.0	472.5	539.0
Phenylpropiolic	17	222.2	300.4	352.0	400.0	470.0	539.0
Dimethylmalonic	17	222.2	300.4	352.0	400.0	470.0	539.0
Ethylmalonic	17	222.2	300.4	352.0	400.0	470.0	539.0
o-Phthalic	18	...	...	...	400.0	470.0	538.8
Sulphanilic	18	222.0*	...	350.9	400.0	470.0	538.8
Metanilic	18	222.0*	...	350.9	400.0	470.0	538.8
Phenylacetic	18	...	...	...	400.0	466.0	535.2
Allylmalonic	18	221.4	299.3	350.9	400.0	468.0	537.0
Cinnamic	19	...	...	...	399.2	470.0	537.2
Dinitroaminophenol	19	221.7	299.1	350.2	399.0	470.0	537.2
Anisic	19	221.7	299.1	350.2	399.0	470.0	577.2
Vanillic	20	221.3	299.1	349.8	397.3	464.0	532.8
Coumaric	20	220.9	298.9	349.8	397.9	468.0	534.4
Methylethylmalonic	20	221.0	299.0	349.8	397.2	464.0	533.0
Isopropylmalonic	20	221.0	299.0	349.8	397.3	464.0	533.0
Hydrocinnamic	21	220.8	298.9	349.7	397.2	463.5	532.6
Acetylsalicylic	21	220.8	297.4	344.4	397.9	463.5	...
Diethylmalonic	23	219.4	296.1	346.2	393.2	464.8	533.9
Butylmalonic	23	219.4	296.1	346.2	393.9	464.8	533.9
Benzylmalonic	24	219.0	295.6	345.7	393.2	464.0	533.0
Napthionic	24	221.9	296.3	352.2	401.1	468.0	534.5
Dipropylmalonic	29	218.6	295.1	345.7	392.8	458.0	520.0

Measurements with bromosuccinic and acetylsalicylic acids could not be completed at higher temperatures, because these acids decomposed.

The sodium salt of dinitroaminophenol could not be made by titration, because of the depth of color of the solution.

No indicator was necessary in the case of coumaric acid—the solution itself turning green when neutralized with sodium hydroxide.

It will be seen from the above table that the values for μ_∞ decrease pretty regularly. A curve, in which the ordinates represent μ_∞ values and the abscissae the number of atoms, shows this relation very nicely. The following diagram was plotted in this manner—μ_∞ values for monobasic acids at 25° and 65° being used as examples.

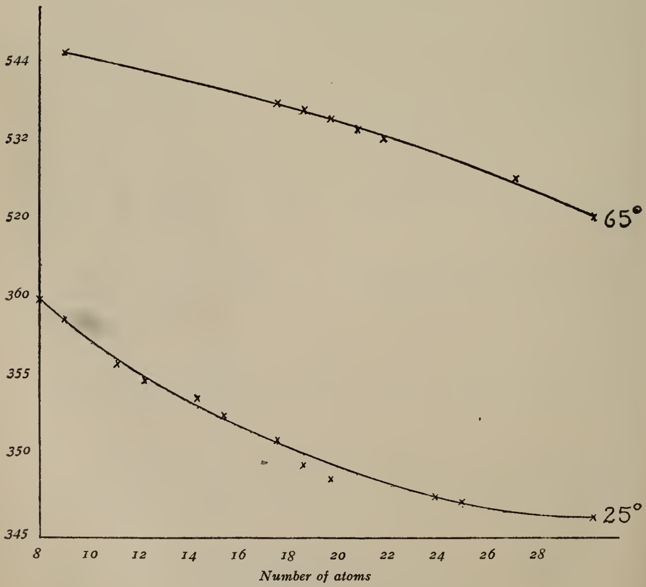


Fig. 1.—Limiting conductivities

Results

The results of our conductivity measurements are tabulated in the following pages. The molecular conductivities (μ_v) are expressed in Siemens' units.

The temperature coefficients expressed in conductivity units = $(\mu_{t_1} - \mu_t)/(t_1 - t)$.

The percentage temperature coefficients = *cond. units*/μ_t where t is the one temperature, t_1 the next higher temperature measured, μ_t and μ_{t_1} the conductivities for the same solution, measured at temperatures t and t_1, respectively.

Percentage dissociation (α) is of course μ_v/μ_∞.

The dissociation constants (K) = $\alpha^2/(1-\alpha)V$, which is the Ostwald dilution law.

Dichloroacetic Acid, $CHCl_2.COOH$

Molecular Conductivity

V	0°	15°	25°	35°	50°	65°
32	166.0	220.3	253.9	286.9	330.8	356.8
128	203.7	272.6	318.0	360.4	418.3	453.3
512	220.5	300.0	352.8	403.8	468.6	528.4
1024	221.7	305.6	359.3	408.7	470.0	535.8
2048	217.0	302.1	358.1	408.5	477.3	545.8

Temperature Coefficients (Cond. Units)

V	0°–15°	15°–25°	25°–35°	35°–50°	50°–65°
32	3.62	3.36	3.30	2.93	1.75
128	4.59	4.54	4.24	3.86	2.33
512	5.30	5.28	5.10	4.19	3.99
1024	5.46	5.37	4.94	4.09	4.39
2048	5.67	5.60	5.04	4.59	4.57

Temperature Coefficients (Per cent.)

V	0°–15°	15°–25°	25°–35°	35°–50°	50°–65°
32	2.18	1.53	1.30	1.02	0.52
128	2.25	1.66	1.33	1.07	0.56
512	2.41	1.76	1.43	1.04	0.87
1024	2.46	1.75	1.37	1.00	0.90
2048	2.61	1.85	1.41	1.12	0.95

Percentage Dissociation

V	0°	15°	25°	35°	50°	65°
32	74.87	72.09	70.67	70.20	69.32	65.37
128	91.88	89.20	88.51	88.12	87.64	83.05
512	99.46	98.17	98.18	98.80	98.18	96.81
1024	100.00	100.00	100.00	100.00	98.47	98.17
2048					100.00	100.00

Phenylacetic Acid, $C_6H_5CH_2.COOH$

Molecular Conductivity

V	35°	50°	65°
32	15.81	17.79	19.26
128	30.68	34.75	37.53
512	58.60	65.64	70.98
1024	78.80	88.31	95.18
2048	106.1	120.0	130.0

Temperature Coefficients

	35°–50°		50°–65°	
V	Cond. units	Per cent.	Cond. units	Per cent.
32	0.132	0.83	0.098	0.55
128	0.260	0.84	0.185	0.49
512	0.470	0.80	0.356	0.54
1024	0.634	0.80	0.451	0.51
2048	0.926	0.87	0.666	0.55

Percentage Dissociation

V	35°	50°	65°
32	3.95	3.86	3.60
128	7.72	7.46	7.01
512	14.65	14.08	13.26
1024	19.70	18.95	17.78
2048	26.53	25.75	24.29

Dissociation Constants

V	35°	50°	65°
32	0.507	0.484	0.420
128	0.505	0.470	0.413
512	0.491	0.451	0.396
1024	0.472	0.433	0.375
2048	0.468	0.436	0.381

Ethylmalonic Acid, $C_2H_5CH(COOH)_2$

Molecular Conductivity

V	0°	15°	25°	35°	50°	65°
8	20.85	28.08	32.62	36.64	41.67	46.09
32	40.90	55.22	64.42	72.53	82.52	90.66
128	73.08	98.35	114.55	129.09	146.60	161.77
512	119.8	161.7	188.9	213.0	243.3	269.9
1024	146.4	197.8	231.2	260.0	297.9	330.6
2048	166.7	125.4	263.5	298.3	345.3	384.7

Temperature Coefficients (Cond. Units)

V	0°–15°	15°–25°	25°–35°	35°–50°	50°–65°
8	0.48	0.45	0.40	0.33	0.29
32	0.95	0.92	0.81	0.67	0.54
128	1.68	1.62	1.45	1.17	1.01
512	2.79	2.72	2.41	2.02	1.64
1024	3.42	3.34	2.88	2.53	2.18
2048	3.91	3.81	3.48	3.13	2.63

Temperature Coefficients (Per cent.)

V	0°–15°	15°–25°	25°–35°	35°–50°	50°–65°
8	2.31	1.61	1.23	0.91	0.71
32	2.33	1.66	1.27	0.92	0.66
128	2.30	1.65	1.26	0.90	0.66
512	2.33	1.68	1.27	0.95	0.67
1024	2.33	1.69	1.25	0.97	0.71
2048	2.35	1.69	1.32	1.04	0.76

Percentage Dissociation

V	0°	15°	25°	35°	50°	65°
8	9.38	9.34	9.27	9.17	8.85	8.55
32	18.41	18.38	18.31	18.15	17.56	16.82
128	32.89	32.73	32.56	32.30	31.20	30.01
512	53.93	53.82	53.70	53.30	51.77	50.08
1024	65.91	65.83	65.72	65.06	63.40	61.34
2048	75.04	75.00	74.91	74.65	73.47	71.37

Dissociation Constants

V	0°	15°	25°	35°	50°	65°
8	12.1	12.0	11.8	11.6	10.7	10.0
32	12.9	12.9	12.8	12.5	11.6	10.6
128	12.6	12.4	12.3	12.0	11.0	10.0
512	12.3	12.2	12.2	11.9	10.9	9.8
1024	12.4	12.3	12.3	11.8	10.7	9.5

Isopropylmalonic Acid, $(CH_3)_2CHCH(COOH)_2$

Molecular Conductivity

V	0°	15°	25°	35°	50°	65°
32	40.07	54.69	64.92	73.63	84.05	91.73
128	72.21	98.65	117.0	132.34	151.88	168.00
512	118.6	161.6	192.9	217.6	248.8	278.4
1024	144.1	197.0	234.0	264.4	307.7	343.8
2048	167.4	228.9	272.2	307.9	357.0	402.5

Temperature Coefficients (Cond. Units)

V	0°–15°	15°–25°	25°–35°	35°–50°	50°–65°
32	0.97	1.02	0.87	0.69	0.51
128	1.76	1.83	1.53	1.30	1.07
512	2.86	3.14	2.47	2.08	1.97
1024	3.53	3.70	3.04	2.89	2.41
2048	4.10	4.32	3.77	3.27	3.03

Temperature Coefficients (Per cent.)

V	0°–15°	15°–25°	25°–35°	35°–50°	50°–65°
32	2.43	1.87	1.34	0.94	0.61
128	2.43	1.86	1.31	0.98	0.71
512	2.41	1.88	1.28	0.96	0.79
1024	2.45	1.88	1.30	0.92	0.78
2048	2.45	1.88	1.38	1.06	0.85

Percentage Dissociation

V	0°	15°	25°	35°	50°	65°
32	18.14	18.29	18.56	18.50	18.11	17.21
128	32.69	33.00	33.45	33.26	32.73	31.52
512	53.70	54.04	55.15	54.69	53.62	53.23
1024	65.24	65.89	66.89	66.44	66.31	64.50
2048	75.79	76.59	77.80	77.30	76.94	75.51

Dissociation Constants

V	0°	15°	25°	35°	50°	65°
32	12.5	12.8	13.2	13.1	12.5	11.2
128	12.4	12.7	13.1	12.9	12.5	11.3
512	12.2	12.4	13.2	12.9	12.1	11.2
1024	12.0	12.4	13.2	12.8	12.5	11.4
2048	11.6	12.2	13.3	12.9	12.5	11.3

Butylmalonic Acid, $C_4H_9CH(COOH)_2$

Molecular Conductivity

V	0°	15°	25°	35°	50°	65°
32	37.53	50.60	58.72	66.30	76.00	83.93
128	68.80	92.04	107.34	121.86	141.00	156.00
512	113.8	154.20	180.9	204.8	236.2	264.2
1024	140.0	187.2	218.3	248.0	286.2	320.1
2048	163.7	218.8	255.4	291.3	340.0	382.6

Temperature Coefficients (Cond. Units)

V	0°–15°	15°–25°	25°–35°	35°–50°	50°–65°
32	0.87	0.81	0.78	0.65	0.53
128	1.55	1.53	1.45	1.28	1.00
512	2.69	2.67	2.39	2.09	1.87
1024	3.15	3.11	2.97	2.55	2.26
2048	3.67	3.66	3.59	3.25	2.84

Temperature Coefficients (Per cent.)

V	0°–15°	15°–25°	25°–35°	35°–50°	50°–65°
32	2.32	1.60	1.32	0.98	0.69
128	2.25	1.66	1.35	1.04	0.71
512	2.36	1.73	1.32	1.02	0.79
1024	2.25	1.66	1.36	1.02	0.79
2048	2.23	1.67	1.40	1.11	0.83

Percentage Dissociation

V	0°	15°	25°	35°	50°	65°
32	17.11	17.09	16.96	16.83	16.35	15.71
128	31.36	31.08	31.00	30.92	30.35	29.21
512	51.88	52.08	52.25	52.00	50.82	49.48
1024	63.82	63.22	63.05	62.96	61.57	60.00
2048	74.62	73.89	73.48	73.95	73.15	71.65

Dissociation Constants

V	0°	15°	25°	35°	50°	65°
32	11.0	11.0	10.8	10.6	10.0	9.15
128	11.2	11.0	10.9	10.8	10.3	9.4
512	10.9	11.0	11.1	11.0	10.2	9.5
1024	11.0	10.6	10.5	10.4	9.6	8.8
2048	10.7	10.2	10.0	10.3	9.7	8.8

Allylmalonic Acid, $CH_2 : CHCH_2CH(COOH)_2$

Molecular Conductivity

V	0°	15°	25°	35°	50°	65°
8	24.25	32.63	37.73	42.26	48.94	53.61
32	45.62	61.58	71.47	80.30	92.02	101.16
128	80.81	109.08	126.33	142.15	164.78	181.65
512	130.5	176.3	204.4	231.0	264.5	293.2
1024	158.9	214.0	248.7	281.0	322.7	358.3
2048	176.4	237.9	277.4	313.8	358.6	401.5

Temperature Coefficients (Cond. Units)

V	0°–15°	15°–25°	25°–35°	35°–50°	50°–65°
8	0.56	0.51	0.45	0.44	0.31
32	1.06	0.99	0.88	0.78	0.61
128	1.88	1.72	1.58	1.51	1.12
512	3.05	2.81	2.66	2.23	1.92
1024	3.67	3.47	3.23	2.78	2.37
2048	4.10	3.95	3.64	2.98	2.86

Temperature Coefficients (Per cent.)

V	0°–15°	15°–25°	25°–35°	35°–50°	50°–65°
8	2.30	1.56	1.20	1.05	0.63
32	2.33	1.60	1.23	0.98	0.66
128	2.33	1.58	1.25	1.06	0.68
512	2.33	1.59	1.30	0.97	0.72
1024	2.31	1.62	1.30	0.99	0.73
2048	2.32	1.66	1.31	0.95	0.79

Percentage Dissociation

V	0°	15°	25°	35°	50°	65°
8	10.95	10.90	10.76	10.56	10.46	9.98
32	20.60	20.57	20.37	20.07	19.66	18.84
128	36.49	36.43	36.01	35.54	35.21	33.82
512	58.93	58.87	58.26	57.75	56.52	54.61
1024	71.77	71.47	70.89	70.25	68.96	66.72
2048	79.65	79.45	79.08	78.46	76.62	74.77

Dissociation Constants

V	0°	15°	25°	35°	50°	65°
8	16.8	16.6	16.2	15.6	15.3	13.8
32	16.7	16.6	16.2	15.7	15.0	13.7
128	16.4	16.3	15.8	15.3	14.9	13.5
512	16.5	16.5	15.9	15.4	14.4	12.8
1024	....	....	....	....	14.9	13.1

Benzylmalonic Acid, $C_6H_5CH_2CH(COOH)_2$

Molecular Conductivity

V	0°	15°	25°	35°	50°	65°
32	45.06	60.54	69.82	78.31	89.05	97.76
128	80.22	107.44	124.99	140.37	160.03	175.82
512	128.3	171.8	199.6	225.1	259.0	285.8
1024	153.0	205.6	239.4	269.6	310.8	345.3
2048	177.7	236.2	273.7	310.0	357.9	395.3

Temperature Coefficients (Cond. Units)

V	0°–15°	15°–25°	25°–35°	35°–50°	50°–65°
32	1.03	0.93	0.85	0.72	0.57
128	1.81	1.75	1.54	1.31	1.05
512	2.90	2.78	2.55	2.26	1.79
1024	3.50	3.38	3.02	2.74	2.30
2048	3.89	3.85	3.64	3.19	2.49

Temperature Coefficients (Per cent.)

V	0°–15°	15°–25°	25°–35°	35°–50°	50°–65°
32	2.29	1.53	1.22	0.91	0.65
128	2.20	1.57	1.23	0.93	0.66
512	2.29	1.61	1.27	1.00	0.69
1024	2.29	1.64	1.26	1.02	0.74
2048	2.19	1.63	1.32	1.04	0.69

Percentage Dissociation

V	0°	15°	25°	35°	50°	65°
32	20.57	20.48	20.19	19.91	19.18	18.33
128	36.63	36.34	36.16	35.70	34.49	32.98
512	58.58	58.11	57.74	57.24	55.81	53.62
1024	69.88	69.56	69.26	68.57	66.98	64.79
2048	81.16	79.89	79.16	78.86	77.14	74.16

Dissociation Constants

V	0°	15°	25°	35°	50°	65°
32	16.6	16.5	16.0	15.5	14.2	12.8
128	16.5	16.2	16.0	15.5	14.1	12.7
512	16.2	15.7	15.4	15.0	13.8	12.1
1024	15.8	15.5	15.2	14.6	13.3	11.7
2048	17.0	15.5	14.7	14.4	12.7	10.4

Dimethylmalonic Acid, $(CH_3)_2C(COOH)_2$

Molecular Conductivity

V	0°	15°	25°	35°	50°	65°
8	16.08	22.06	25.83	29.27	34.10	38.13
32	32.00	43.76	51.23	58.41	68.80	77.10
128	59.00	80.57	94.61	107.29	124.82	139.53
512	101.4	136.9	160.2	182.5	217.2	240.7
1024	124.1	169.7	198.9	226.0	266.7	299.3
2048	151.9	205.7	241.1	273.7	314.71	349.5

Temperature Coefficients (Cond. Units)

V	0°–15°	15°–25°	25°–35°	35°–50°	50°–65°
8	0.40	0.38	0.34	0.32	0.27
32	0.78	0.75	0.72	0.69	0.55
128	1.44	1.40	1.27	1.17	0.98
512	2.37	2.33	2.22	2.13	1.57
1024	3.04	2.92	2.71	2.71	2.17
2048	3.59	3.54	3.26	2.74	2.32

Temperature Coefficients (Per cent.)

V	0°–15°	15°–25°	25°–35°	35°–50°	50°–65°
8	2.44	1.70	1.34	1.08	0.79
32	2.43	1.70	1.40	1.18	0.80
128	2.42	1.74	1.34	1.09	0.79
512	2.33	1.70	1.38	1.17	0.72
1024	2.45	1.72	1.36	1.18	0.82
2048	2.36	1.72	1.35	1.00	0.74

Percentage Dissociation

V	0°	15°	25°	35°	50°	65°
8	7.24	7.35	7.34	7.32	7.25	7.07
32	14.40	14.59	14.56	14.62	14.63	14.30
128	26.55	26.86	26.89	26.85	26.56	25.88
512	45.64	45.65	45.56	45.66	46.17	44.66
1024	55.85	56.58	56.55	56.56	56.72	55.52
2048	68.36	68.57	68.53	68.48	67.00	64.85

Dissociation Constants

V	0°	15°	25°	35°	50°	65°
8	7.06	7.28	7.27	7.27	7.08	6.72
32	7.57	7.79	7.75	7.82	7.82	7.45
128	7.50	7.71	7.73	7.70	7.51	7.06
512	7.48	7.49	7.45	7.50	7.69	7.04
1024	6.90	7.20	7.21	7.20	7.26	6.77
2048	7.21	7.30	7.29	7.28	6.64	5.84

Methylethylmalonic Acid, $CH_3(C_2H_5)C(COOH)_2$

Molecular Conductivity

V	0°	15°	25°	35°	50°	65°
8	23.60	31.90	37.34	42.22	48.28	54.11
32	45.89	61.89	72.45	82.00	93.61	104.35
128	81.39	110.44	129.71	147.18	168.51	188.20
512	129.9	176.0	206.3	234.0	269.5	304.3
1024	156.2	211.2	248.2	280.0	323.2	365.5
2048	178.2	240.3	280.6	315.1	365.5	411.6

Temperature Coefficients (Cond. Units)

V	0°–15°	15°–25°	25°–35°	35°–50°	50°–65°
8	0.55	0.54	0.49	0.40	0.39
32	1.07	1.06	0.95	0.77	0.72
128	1.94	1.93	1.75	1.42	1.31
512	3.07	3.04	2.77	2.37	2.32
1024	3.67	3.69	3.18	2.88	2.82
2048	4.14	4.03	3.44	3.36	3.07

Temperature Coefficients (Per cent.)

V	0°–15°	15°–25°	25°–35°	35°–50°	50°–65°
8	2.34	1.70	1.30	0.96	0.72
32	2.33	1.71	1.31	0.94	0.76
128	2.38	1.74	1.34	0.96	0.77
512	2.36	1.72	1.34	1.01	0.85
1024	2.35	1.75	1.28	1.02	0.87
2048	2.32	1.70	1.23	1.07	0.83

Percentage Dissociation

V	0°	15°	25°	35°	50°	65°
8	10.68	10.67	10.67	10.61	10.39	10.15
31	20.78	20.70	20.71	20.61	20.17	19.58
128	36.85	36.94	37.08	36.99	36.31	35.31
512	58.84	58.85	58.99	58.81	59.08	57.08
1024	70.73	70.66	70.96	70.37	69.65	68.58
2048	80.68	80.38	80.25	79.18	78.76	77.22

Dissociation Constants

V	0°	15°	25°	35°	50°	65°
8	16.0	15.9	15.9	15.7	15.6	14.3
32	17.0	16.9	16.9	16.7	15.9	14.5
128	16.8	16.9	17.1	17.0	16.1	15.0
512	16.4	16.4	16.6	16.4	15.7	14.8
1024	16.7	16.6	16.9	16.3	15.6	14.6
2048	16.5	16.1	15.9	15.0	14.3	12.8

Diethylmalonic Acid, $(C_2H_5)_2C(COOH)_2$

Molecular Conductivity

V	0°	15°	25°	35°	50°	65°
8	52.38	67.87	76.92	84.66	94.03	100.32
32	92.77	121.64	138.84	153.60	174.26	186.22
128	141.8	187.3	215.3	240.2	275.0	299.0
512	189.0	252.3	292.2	328.7	378.8	422.6
1024	201.2	268.2	312.0	353.6	413.7	462.8
2048	201.6	272.2	317.2	360.5	424.4	471.6

Temperature Coefficients (Cond. Units)

V	0°–15°	15°–25°	25°–35°	35°–50°	50°–65°
8	1.03	0.90	0.77	0.72	0.42
32	1.92	1.72	1.48	1.38	0.80
128	3.04	2.80	2.49	2.33	1.67
512	4.22	3.99	3.65	3.34	2.92
1024	4.47	4.37	4.16	4.01	3.27
2048	4.71	4.50	4.32	4.26	3.83

Temperature Coefficients (Per cent.)

V	0°–15°	15°–25°	25°–35°	35°–50	50°–65°
8	1.97	1.33	1.00	0.85	0.44
32	2.07	1.41	1.06	0.89	0.46
128	2.14	1.49	1.15	0.97	0.61
512	2.23	1.58	1.25	1.01	0.77
1024	2.22	1.63	1.33	1.13	0.79
2048	2.33	1.65	1.36	1.18	0.90

Percentage Dissociation

V	0°	15°	25°	35°	50°	65°
8	23.88	22.92	22.22	21.49	20.23	18.79
32	42.29	41.08	40.10	39.00	37.49	34.87
128	64.65	63.27	62.19	60.98	59.15	56.00
512	86.17	85.21	84.40	83.46	81.56	79.14
1024	91.73	90.59	90.10	89.76	89.00	86.66
2048	91.92	91.94	91.62	91.52	91.30	88.32

Dipropylmalonic Acid, $(C_3H_7)_2C(COOH)_2$

Molecular Conductivity

V	0°	15°	25°	35°	50°	65°
32	103.2	135.1	154.5	170.3	...	...
128	152.2	204.4	234.9	261.7	297.5	304.2
512	192.1	258.8	300.6	339.3	386.5	430.1
1024	203.5	272.9	317.8	359.1	417.0	468.0
2048	209.3	281.1	328.9	373.0	434.6	490.9

Temperature Coefficients (Cond. Units)

V	0°–15°	15°–25°	25°–35°	35°–50°	50°–65°
32	2.13	1.94	1.58	....	....
128	3.47	3.06	2.68	2.39	1.78
512	4.45	4.18	3.86	3.15	2.95
1024	4.63	4.49	4.14	3.86	3.40
2048	4.78	4.78	4.41	4.11	3.75

Temperature Coefficients (Per cent.)

V	0°–15°	15°–25°	25°–35°	35°–50°	50°–65°
32	2.06	1.41	1.02	....	....
128	2.28	1.49	1.14	0.91	0.60
512	2.31	1.62	1.28	0.93	0.74
1024	2.27	1.64	1.30	1.09	0.81
2048	2.29	1.70	1.34	1.10	0.86

Percentage Dissociation

V	0°	15°	25°	35°	50°	65°
32	47.18	45.78	44.70	43.35	...	...
128	69.63	69.25	67.95	66.60	64.96	62.34
512	87.85	87.70	86.97	86.35	84.40	82.77
1024	93.07	92.48	91.92	91.41	91.06	90.00
2048	95.74	95.26	95.15	94.93	94.89	94.40

Dissociation Constants

V	0°	15°	25°	35°	50°	65°
32	132	121	113	104	..	..
128	125	121	113	104	90	81
512	124	122	113	106	89	78
1024	122	111	102	95	90	79
2048	105	93	91	90	90	78

Bromosuccinic Acid, $HOOCCHBrCH_2COOH$

Molecular Conductivity

V	0°	15°	25°
128	101.46	136.01	158.19
512	156.00	210.27	246.72
1024	189.44	252.44	293.74
2048	208.37	283.02	328.50

Temperature Coefficients

	0°–15°		15°–25°	
V	Cond units.	Per cent.	Cond units.	Per cent.
128	2.30	2.27	2.21	1.60
512	3.62	2.32	3.60	1.62
1024	4.20	2.22	4.13	1.60
2048	4.71	2.26	4.55	1.61

Percentage Dissociation

V	0°	15°	25°
128	45.66	45.02	44.67
512	70.20	70.40	69.66
1024	85.25	83.55	82.94
2048	93.77	93.67	92.76

Dissociation Constants

V	0°	15°	25°
128	30	29	28
512	32	33	31
1024	48	41	39
2048	69	68	58

Dibromosuccinic Acid, HOOCCHBrCHBrCOOH

Molecular Conductivity

V	0°	15°	25°	35°	50°	65°
32	175.6	222.2	245.6	262.9	293.4	342.6
128	254.3	326.8	367.6	399.7	448.6	509.8
512	339.1	438.4	497.4	546.5	615.0	685.9
1024	381.6	501.8	571.4	635.0	707.1	786.1
2048	416.1	550.0	631.9	704.9	792.2	879.4

Temperature Coefficients (Cond. Units)

V	0°–15°	15°–25°	25°–35°	35°–50°	50°–65°
32	3.10	2.34	1.74	2.03	3.28
128	4.83	4.07	3.21	3.26	4.08
512	6.62	5.99	4.91	4.56	4.73
1024	8.01	6.96	6.35	4.81	5.26
2048	8.92	8.19	7.39	5.82	5.82

Temperature Coefficients (Per cent.)

V	0°–15°	15°–25°	25°–35°	35°–50°	50°–65°
32	1.77	1.05	0.71	0.77	1.09
128	1.89	1.24	0.87	0.82	0.91
512	1.95	1.34	0.98	0.83	0.77
1024	2.10	1.39	1.11	0.76	0.74
2048	2.14	1.49	1.15	0.83	0.73

Pyromucic Acid, C_4H_3OCOOH

Molecular Conductivity

V	35°	50°	65°
8	28.59	31.59	33.36
32	56.36	62.36	66.56
128	105.01	116.32	124.38
512	179.4	199.9	213.8
1024	223.0	249.2	265.3
2048	269.2	308.9	333.9

Temperature Coefficients

	35°–50°		50°–65°	
V	Cond. units	Per cent.	Cond. units	Per cent.
8	0.20	0.70	0.12	0.37
32	0.40	0.71	0.28	0.45
128	0.75	0.72	0.54	0.46
512	1.37	0.76	0.93	0.46
1024	1.78	0.79	1.07	0.43
2048	2.65	0.98	1.67	0.54

Percentage Dissociation

v	35°	50°	65°
8	7.07	6.71	6.19
32	13.93	13.24	12.34
128	25.96	24.69	23.07
512	44.35	42.44	39.65
1024	55.13	52.91	49.20
2048	66.55	65.58	61.93

Dissociation Constants

v	35°	50°	65°
8	6.7	6.0	5.1
23	7.0	6.3	5.4
128	7.1	6.3	5.4
512	6.9	6.1	5.1
1024	6.6	5.8	4.8
2048	6.5	6.1	4.9

Phenylpropiolic Acid, $C_6H_5C : CCOOH$

Molecular Conductivity

v	0°	15°	25°	35°	50°	65°
128	132.6	177.0	203.3	227.2	255.6	274.7
256	154.8	208.0	239.2	267.6	301.2	327.4
512	176.1	236.6	274.4	307.8	349.7	375.3
1024	191.4	258.0	299.8	339.2	392.1	422.1
2048	200.5	269.0	314.8	357.9	416.6	449.6

Temperature Coefficients (Cond. Units)

v	0°–15°	15°–25°	25°–35°	35°–50°	50°–65°
128	2.96	2.63	2.39	1.89	1.27
256	3.54	3.12	2.84	2.24	1.53
512	4.05	3.78	3.34	2.77	1.71
1024	4.44	4.08	3.94	3.53	2.00
2048	4.56	4.58	4.31	3.91	2.20

Temperature Coefficients (Per cent.)

v	0°–15°	15°–25°	25°–35°	35°–50°	50°–65°
128	2.23	1.48	1.17	0.83	0.50
256	2.24	1.50	1.18	0.84	0.51
512	2.25	1.59	1.21	0.90	0.49
1024	2.32	1.62	1.31	1.04	0.51
2048	2.27	1.70	1.36	1.09	0.53

Percentage Dissociation

V	0°	15°	25°	35°	50°	65°
128	59.67	58.91	57.87	56.82	54.39	50.98
256	69.66	69.22	68.08	66.90	64.09	60.76
512	79.24	78.76	78.12	76.97	74.41	69.66
1024	86.15	85.89	85.34	84.81	83.43	78.35
2048	90.25	89.54	89.60	89.48	88.63	83.43

Dissociation Constants

V	0°	15°	25°	35°	50°	65°
128	68.9	66.0	62.1	58.4	50.7	41.4
256	62.5	60.8	56.7	52.8	44.7	36.8
512	59.1	57.0	54.5	50.2	42.3	31.2
1024	52.3	51.1	48.5	46.2	41.0	27.7
2048	40.8	37.4	37.7	37.2	33.7	20.5

Salicylic Acid, HOC_6H_4COOH

Molecular Conductivity

V	35°	50°	65°
64	93.64	110.55	124.60
128	125.96	148.72	166.80
512	209.7	249.1	280.1
1024	255.0	301.7	337.2
2048	294.6	350.1	392.6

Temperature Coefficients

	35°–50°		50°–65°	
V	Cond. units	Per cent.	Cond. units	Per cent.
64	1.13	1.21	0.94	0.85
128	1.52	1.21	1.20	0.81
512	2.63	1.25	2.07	0.83
1024	3.11	1.22	2.37	0.79
2048	3.70	1.25	2.77	0.79

Percentage Dissociation

V	35°	50°	65°
64	23.24	23.37	23.13
128	31.26	31.44	30.96
512	52.05	52.67	52.00
1024	63.29	63.78	62.58
2048	73.12	74.01	72.87

Dissociation Constants

V	35°	50°	65°
64	11.0	11.1	10.9
128	11.1	11.2	10.8
512	11.0	11.4	11.0
1024	10.7	11.0	10.2

Acetylsalicylic Acid, $CH_3COOC_6H_4COOH$

Molecular Conductivity

V	0°	15°	25°	35°	50°
128	40.40	52.78	60.60	68.89	79.41
512	73.10	95.21	109.27	124.34	142.88
1024	92.60	121.0	139.3	158.7	184.1
2048	118.1	154.5	177.6	205.1	238.3

Temperature Coefficients (Cond. Units)

V	0°–15°	15°–25°	25°–35°	35°–50°
128	0.83	0.78	0.83	0.70
512	1.47	1.41	1.51	1.24
1024	1.89	1.83	1.94	1.69
2048	2.43	2.30	2.75	2.35

Temperature Coefficients (Per cent.)

V	0°–15°	15°–25°	25°–35°	35°–50°
128	2.04	1.48	1.37	1.02
512	2.01	1.48	1.38	1.00
1024	2.04	1.51	1.39	1.06
2048	2.14	1.49	1.54	1.14

Percentage Dissociation

V	0°	15°	25°	35°	50°
128	18.30	17.75	17.59	17.31	17.13
512	33.11	32.00	31.73	31.25	30.82
1024	41.49	40.68	40.45	39.89	39.72
2048	53.50	51.95	51.55	51.54	51.42

Dissociation Constants

V	0°	15°	25°	35°	50°
128	3 2	3.0	2.9	2.8	2.7
512	3.2	2.9	2.9	2.8	2.7
1024	3.0	2.7	2.7	2.6	2.6
2048	3.0	2.7	2.7	2.7	2.7

Sulphosalicylic Acid, $HOC_6H_3(SO_3H)COOH$

Molecular Conductivity

V	0°	15°	25°	35°	50°	65°
32	209.4	283.7	332.0	377.6	432.9	486.8
128	239.6	328.5	386.5	440.1	508.9	575.4
512	291.9	403.3	474.1	538.5	622.4	706.2
1024	322.5	443.0	522.4	598.1	701.3	785.7
2048	352.0	485.0	570.4	651.7	762.3	858.0

Temperature Coefficients (Cond. Units)

V	0°–15°	15°–25°	25°–35°	35°–50°	50°–65°
32	4.95	4.83	4.56	3.69	3.59
128	5.93	5.79	5.36	4.61	4.43
512	7.42	7.08	6.44	5.59	5.58
1024	8.04	7.93	7.57	6.84	5.62
2048	8.87	8.54	8.13	7.38	6.38

Temperature Coefficients (Per cent.)

V	0°–15°	15°–25°	25°–35°	35°–50°	50°–65°
32	2.36	1.70	1.37	0.98	0.83
128	2.47	1.76	1.38	1.05	0.87
512	2.54	1.75	1.35	1.04	0.89
1024	2.49	1.79	1.44	1.14	0.81
2048	2.51	1.76	1.42	1.13	0.84

Anisic Acid, $CH_3OC_6H_4COOH$

Molecular Conductivity

V	0°	15°	25°	35°	50°	65°
1024	35.80	50.50	59.10	67.60	80.29	90.25
2048	47.13	66.74	78.80	90.15	103.67	115.17

Temperature Coefficients (Cond. Units)

V	0°–15°	15°–25°	25°–35°	35°–50°	50°–65°
1024	0.98	0.86	0.85	0.84	0.66
2048	1.31	1.20	1.13	0.90	0.77

Temperature Coefficients (Per cent.)

V	0°–15°	15°–25°	25°–35°	35°–50°	50°–65°
1024	2.74	1.70	1.43	1.24	0.82
2048	2.77	1.80	1.43	1.00	0.74

Percentage Dissociation

V	0°	15°	25°	35°	50°	65°
1024	16.14	16.84	16.88	16.94	17.06	16.80
2048	21.26	22.25	22.50	22.59	22.03	21.44

Dissociation Constants

V	0°	15°	25°	35°	50°	65°
1024	0.303	0.333	0.335	0.337	0.343	0.331
2048	0.280	0.311	0.319	0.322	0.304	0.285

Vanillic Acid, $CH_3OC_6H_3(OH)COOH$

Molecular Conductivity

V	0°	15°	25°	35°	50°	65°
256	18.48	26.44	31.68	36.49	42.32	47.41
512	26.16	36.65	43.30	49.89	57.80	64.62
1024	35.87	50.10	59.55	69.00	80.38	89.42
2048	47.26	67.40	80.88	93.48	109.15	120.08

Temperature Coefficients (Cond. Units)

V	0°–15°	15°–25°	25°–35°	35°–50°	50°–65°
256	0.53	0.52	0.48	0.39	0.34
512	0.70	0.66	0.66	0.53	0.45
1024	0.95	0.95	0.94	0.76	0.60
2048	1.34	1.34	1.26	1.04	0.73

Temperature Coefficients (Per cent.)

V	0°–15°	15°–25°	25°–35°	35°–50°	50°–65°
256	2.87	1.98	1.52	1.07	0.80
512	2.67	1.81	1.52	1.06	0.79
1024	2.63	1.88	1.58	1.10	0.75
2048	2.80	1.99	1.55	1.11	0.67

Percentage Dissociation

V	0°	15°	25°	35°	50°	65°
256	8.35	8.84	9.05	9.18	9.12	8.90
512	11.82	12.25	12.38	12.56	12.46	12.13
1024	16.21	16.75	17.33	17.37	17.32	16.78
2048	21.35	22.53	23.12	23.53	23.52	22.54

Dissociation Constants

V	0°	15°	25°	35°	50°	65°
256	0.30	0.33	0.35	0.36	0.36	0.34
512	0.31	0.33	0.34	0.35	0.35	0.33
1024	0.31	0.33	0.35	0.36	0.35	0.33
2048	0.28	0.32	0.34	0.35	0.35	0.32

Metanilic Acid, $H_2NC_6H_4SO_3H$

Molecular Conductivity

V	35°	50°	65°
32	35.37	49.48	66.05
128	66.86	92.74	123.89
512	122.35	165.15	216.84
1024	158.2	210.0	267.3
2048	202.4	264.3	331.7

Temperature Coefficients

	35°–50°		50°–65°	
V	Cond. units	Per cent.	Cond. units	Per cent.
32	0.94	2.66	1.10	2.23
128	1.72	2.57	2.08	2.24
512	2.85	2.33	3.44	2.09
1024	3.45	2.18	3.82	1.81
2048	4.13	2.04	4.49	1.63

Percentage Dissociation

V	35°	50°	65°
32	8.84	10.53	12.25
128	16.72	19.73	22.99
512	30.58	35.14	40.24
1024	39.55	44.68	49.61
2048	50.60	56.23	61.56

Dissociation Constants

V	35°	50°	65°
32	2.68	3.87	5.34
128	2.62	3.80	5.36
512	2.63	3.72	5.29
1024	2.53	3.52	4.79
2048	2.53	3.53	4.81

Sulphanilic Acid, $H_2NC_6H_4SO_3H$

Molecular Conductivity

V	25°	35°	50°	65°
32	45.39	58.35	78.23	100.50
128	85.40	107.80	145.00	186.40
512	148.66	180.88	237.00	298.00
1024	182.8	221.6	287.0	352.6
2048	223.0	268.0	336.8	406.7

Temperature Coefficients (Cond. Units)

	25°–35°		35°–50°		50°–65°	
V	Cond. units	Per cent.	Cond. units	Per cent.	Cond. units	Per cent.
32	1.30	2.68	1.33	2.28	1.48	1.89
128	2.24	2.62	2.48	2.30	2.73	1.88
512	3.22	2.17	3.73	2.06	4.07	1.72
1024	3.88	2.12	4.36	1.97	4.37	1.52
2048	4.50	2.02	4.58	1.71	4.66	1.38

Percentage Dissociation

V	25°	35°	50°	65°
32	12.94	14.59	16.64	18.65
128	24.34	26.95	30.85	34.59
512	41.79	45.22	50.42	55.30
1024	52.08	55.40	61.06	65.44
2048	63.52	67.00	71.65	75.48

Dissociation Constants

V	25°	35°	50°	65°
32	6.01	7.78	10.4	13.4
128	6.09	7.77	10.7	14.2
512	5.86	7.30	10.0	13.4
1024	5.53	6.72	9.35	12.1
2048	5.40	6.64	8.84	11.3

4,6-Dinitro-2-aminophenol, $(O_2N)_2C_6H_2(NH_2)OH$

Molecular Conductivity

V	0°	15°	25°	35°	50°	65°
512	24.00	39.78	51.80	64.93	85.67	110.8
1024	32.90	54.09	70.16	88.60	119.00	153.5
2048	44.60	73.80	95.20	119.7	161.8	208.4

Temperature Coefficients (Cond. Units)

V	0°–15°	15°–25°	25°–35°	35°–50°	50°–65°
512	1.05	1.20	1.31	1.38	1.67
1024	1.41	1.61	1.84	2.02	2.30
2048	1.95	2.26	2.45	2.80	3.11

Temperature Coefficients (Per cent.)

V	0°–15°	15°–25°	25°–35°	35°–50°	50°–65°
512	4.37	3.02	2.53	2.12	1.94
1024	4.30	2.97	2.58	2.28	1.93
2048	4.37	3.10	2.57	2.34	1.92

Percentage Dissociation

V	0°	15°	25°	35°	50°	65°
512	10.82	13.30	14.73	16.27	18.22	20.62
1024	14.84	18.08	19.95	22.20	25.32	28.57
2048	20.10	24.61	27.20	29.93	34.42	38.79

Dissociation Constants

V	0°	15°	25°	35°	50°	65°
512	0.256	0.398	0.497	0.617	0.793	1.05
1024	0.253	0.389	0.486	0.619	0.838	1.11
2048	0.247	0.392	0.496	0.624	0.882	1.20

Hydrocinnamic Acid, $C_6H_5CH_2CH_2COOH$

Molecular Conductivity

V	0°	15°	25°	35°	50°	65°
32	5.89	8.07	9.40	10.57	11.81	13.00
128	11.49	15.64	18.32	20.56	23.20	25.28
512	22.18	30.46	35.49	39.85	44.82	49.00
1024	30.40	41.76	48.84	54.79	61.37	67.04
2048	41.60	56.41	65.65	73.72	83.02	89.66

Temperature Coefficients (Cond. Units)

V	0°–15°	15°–25°	25°–35°	35°–50°	50°–65°
32	0.145	0.133	0.104	0.083	0.079
128	0.276	0.268	0.224	0.176	0.138
512	0.552	0.503	0.436	0.331	0.278
1024	0.757	0.708	0.595	0.438	0.378
2048	0.987	0.923	0.807	0.620	0.443

Temperature Coefficients (Per cent.)

V	0°–15°	15°–25°	25°–35°	35°–50°	50°–65°
32	2.47	1.65	1.24	0.78	0.67
128	2.41	1.71	1.22	0.85	0.59
512	2.49	1.65	1.23	0.83	0.62
1024	2.49	1.69	1.22	0.80	0.61
2048	2.37	1.64	1.23	0.84	0.53

Percentage Dissociation

V	0°	15°	25°	35°	50°	65°
32	2.67	2.70	2.69	2.66	2.55	2.44
128	5.20	5.23	5.23	5.17	5.01	4.75
512	10.04	10.17	10.14	10.03	9.67	9.20
1024	13.76	13.97	13.96	13.79	13.24	12.59
2048	18.84	18.87	18.77	18.56	17.91	16.83

Dissociation Constants

V	0°	15°	25°	35°	50°	65°
32	0.229	0.234	0.232	0.227	0.208	0.191
128	0.223	0.225	0.225	0.220	0.206	0.185
512	0.219	0.225	0.223	0.218	0.202	0.182
1024	0.214	0.222	0.221	0.215	0.197	0.177
2048	0.214	0.214	0.212	0.205	0.191	0.166

Cinnamic Acid, $C_6H_5CH : CHCOOH$

Molecular Conductivity

V	35°	50°	65°
512	51.10	59.90	67.02
1024	69.40	80.93	90.20
2048	95.25	111.00	124.00

Temperature Coefficients

	35°–50°		50°–65°	
V	Cond. units	Per cent.	Cond. units	Per cent.
512	0.58	1.13	0.47	0.79
1024	0.77	1.11	0.62	0.77
2048	1.05	1.10	0.87	0.78

Percentage Dissociation

V	35°	50°	65°
512	12.80	12.74	12.48
1024	17.38	17.22	16.79
2048	23.86	23.62	23.08

Dissociation Constants

V	35°	50°	65°
512	0.367	0.363	0.347
1024	0.357	0.350	0.331
2048	0.365	0.357	0.338

o-*Coumaric Acid, $HOC_6H_4CH : CHCOOH$*

Molecular Conductivity

V	0°	15°	25°	35°	50°	65°
256	16.00	23.22	27.08	30.38	35.56	39.39
512	22.40	32.39	37.58	42.01	49.08	54.24
1024	31.48	46.00	53.38	59.52	69.57	76.92
2048	44.53	65.13	75.56	77.50	90.50	98.75

Temperature Coefficients (Cond. Units)

V	0°–15°	15°–25°	25°–35°	35°–50°	50°–65°
256	0.48	0.38	0.33	0.34	0.25
512	0.67	0.52	0.44	0.47	0.34
1024	0.97	0.74	0.61	0.67	0.49
2048	1.38	1.04	0.19	0.87	0.55

Temperature Coefficients (Per cent.)

V	0°–15°	15°–25°	25°–35°	35°–50°	50°–65°
256	3.00	1.64	1.21	1.13	0.71
512	2.99	1.61	1.18	1.12	0.70
1024	3.07	1.63	1.15	1.12	0.70
2048	3.08	1.60	0.25	1.12	0.61

Percentage Dissociation

V	0°	15°	25°	35°	50°	65°
256	7.27	7.74	7.73	7.60	7.59	7.37
512	10.18	10.80	10.74	10.51	10.48	10.15
1024	14.30	15.34	15.25	14.89	14.86	14.39
2048	20.23	21.72	21.59	19.39	19.34	18.48

Dissociation Constants

V	0°	15°	25°	35°	50°	65°
256	0.223	0.254	0.253	0.244	0.243	0.229
512	0.225	0.255	0.252	0.241	0.240	0.224
1024	0.233	0.271	0.268	0.254	0.252	0.236
2048	0.250	0.294	0.290	0.228	0.226	0.205

o-*Phthalic Acid*, $C_6H_4(COOH)_2$

Molecular Conductivity

V	35°	50°	65°
64	96.31	110.20	122.70
128	128.06	147.58	163.86
512	212.8	244.8	272.4
1024	258.5	300.3	336.9
2048	302.7	352.7	395.1

Temperature Coefficients

	35°–50°		50°–65°	
V	Cond. units	Per cent.	Cond. units	Per cent.
64	0.93	0.96	0.83	0.75
128	1.30	1.02	1.09	0.74
512	2.13	1.01	1.84	0.75
1024	2.78	1.08	2.44	0.81
2048	3.33	1.10	2.83	0.80

Percentage Dissociation

V	35°	50°	65°
64	24.08	23.45	22.77
128	32.01	31.40	30.41
512	53.20	52.09	50.55
1024	64.62	63.89	62.53
2048	75.68	75.04	73.33

Dissociation Constants

V	35°	50°	65°
64	11.9	11.2	10.5
128	11.8	11.2	10.4
512	11.8	11.1	10.1
1024	11.5	11.0	10.2
2048	11.5	11.0	9.8

Naphthionic Acid, $C_{10}H_6(NH_2)SO_3H$

Molecular Conductivity

V	0°	15°	25°	35°	50°	65°
1024	142.2	212.7	262.0	312.9	382.6	450.6
2048	169.8	245.5	295.4	347.2	420.9	491.2

Temperature Coefficients (Cond. Units)

V	0°–15°	15°–25°	25°–35°	35°–50°	50°–65°
1024	4.70	4.93	5.09	4.64	4.56
2048	5.05	4.99	5.16	4.92	4.68

Temperature Coefficients (Per cent.)

V	0°–15°	15°–25°	25°–35°	35°–50°	50°–65°
1024	3.30	2.32	1.94	1.48	1.19
2048	3.00	2.03	1.48	1.42	1.11

Percentage Dissociation

V	0°	15°	25°	35°	50°	65°
1024	64.04	71.82	74.43	78.23	81.75	84.29
2048	76.58	82.98	83.92	86.80	89.94	91.90

Dissociation Constants

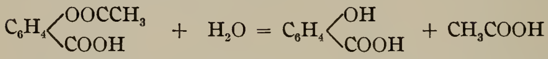
V	0°	15°	25°	35°	50°	65°
1024	11.1	17.9	21.2	27.4	35.8	44.2
2048	12.2	19.7	21.4	27.9	39.3	50.9

The conductivities of bromosuccinic and acetylsalicylic acids could not be measured at higher temperatures. Both acids showed marked evidence of decomposition.

The time factor for the decomposition of bromosuccinic acid is striking.

V	Time	μ_v 35°
1024	30 minutes	442
	45 minutes	458
	1 hour	466
	1.5 hours	472

Acetylsalicylic acid in all probability gives salicylic and acetic acids as a result of hydrolysis:



$$\mathrm{C_6H_4}\Big\langle\begin{matrix}\mathrm{OOCCH_3}\\ \mathrm{COOH}\end{matrix} + \mathrm{H_2O} = \mathrm{C_6H_4}\Big\langle\begin{matrix}\mathrm{OH}\\ \mathrm{COOH}\end{matrix} + \mathrm{CH_3COOH}$$

The velocity of this reaction may be observed in the following data:

V	Time	μ_v 65°
128	35 minutes	93.8
	45 minutes	94.9
	1 hour, 10 minutes	97.3
	2 hours, 15 minutes	105.8
	3 hours	111.0

Possibly the weakening action of the substituting acetyl group in this acid finds its explanation here. We would expect acetylsalicylic acid, under ordinary conditions, to be stronger than salicylic acid. The acetyl derivatives of propionic[1] and aminobenzoic[2] acids are stronger than the original unsubstituted acids. Since, however, acetylsalicylic acid shows such marked evidence of hydrolysis, we think it fair to assume that its small conductivity is due to its great hydrating power.

The μ_∞ values for sulphosalicylic and dibromosucccinic acids, as has already been explained in connection with the table of limiting conductivities, could not be calculated. Therefore, the percentage dissociation and dissociation constants of these acids are not given.

The case of diethylmalonic acid is exceptional. The molecular conductivities at $V = 1024$ and $V = 2048$ are so nearly

[1] THIS JOURNAL, **46**, 78.

[2] Z. physik. Chem., **3**, 263.

Dissociation Constants, K × 10⁴

Acid	0°	15°	25°	35°	50°	65°
Phenylacetic	0.540[1]	....	0.545[1]	0.506	0.477	0.416
Ethylmalonic	12.5	12.4	12.3	11.9	11.0	10.0
Isopropylmalonic	12.3	12.5	13.2	12.9	12.5	11.3
Butylmalonic	11.0	10.9	10.8	10.6	10.2	9.4
Allylmalonic	16.6	16.5	16.0	15.5	14.9	13.4
Benzylmalonic	16.4	15.9	15.0	15.0	13.6	12.0
Diethylmalonic	7.29	7.46	7.45	7.46	7.33	7.01
Methylethylmalonic	16.6	16.5	16.5	16.2	15.8	14.6
Diethylmalonic	88.0	80.0	74.0	69.0	60.0	50.0
Dipropylmalonic	124.0	121.0	113.0	104.0	90.0	79.0
Pyromucic	8.7[1]	....	7.6[1]	6.8	6.1	5.1
Salicylic	8.3[1]	....	10.6[1]	10.9	11.2	10.7
Acetylsalicylic	3.10	2.82	2.80	2.72	2.67	....
Anisic	0.291	0.322	0.327	0.330	0.324	0.308
Vanillic	0.300	0.330	0.345	0.355	0.353	0.330
Metanilic	0.90[1]	....	1.99[1]	2.64	3.80	5.33
Sulphanilic	3.28[1]	....	6.05	7.77	10.4	13.4
Dinitroaminophenol	0.252	0.393	0.493	0.62	0.84	1.12
Hydrocinnamic	0.220	0.224	0.223	0.217	0.206	0.186
Cinnamic	0.322[1]	....	0.368[1]	0.363	0.357	0.339
Coumaric	0.233	0.269	0.266	0.242	0.240	0.224
Phthalic	13.4[1]	....	12.6[1]	11.7	11.1	10.2
Naphthionic	11.7	18.8	21.3	27.6	37.5	47.5

[1] These constants at lower temperatures were calculated by White and Jones: THIS JOURNAL, **44**, 159 (1910).

alike that we might imagine the acid to be almost completely dissociated at these dilutions. Calculated in the usual manner, however, the μ_∞ values do not agree with these. Take for example, μ_∞ at 0° for an acid with 23 atoms, $\mu_\infty = 219.4$. In the case of diethylmalonic acid the experimentally obtained $\mu_\infty = 201.6$. Dissociation constants calculated on the basis of the theoretical μ_∞ scarcely deserve the name of "constants," and are, therefore, omitted from our list.

Owing to the fact that the Ostwald dilution law does not hold for strong acids, many "dissociation constants" belonging to acids of this class are omitted. Some that are given are extremely irregular, and are only of value inasmuch as they indicate the relative strengths of the acids.

In the above table are the probable dissociation constants of most of the acids with which we worked.

Several investigators, who had not made measurements at such high temperatures, observed that while most of the percentage dissociations of organic acids decreased with rising temperature, some of them persistently increased. This increase, however, continued at a diminishing rate. The maximum dissociation has been reached in our work in every case except for the amino acids—sulphanilic, metanilic, naphthionic, dinitroaminophenol. The next class of acids for which the dissociation increased over a wide range in temperature were those acids related to hydroxybenzoic—salicylic, anisic and vanillic acids. These attained maximum dissociation at 35°.

The above mentioned amino acids conform to the observations of White and Jones. Their percentage temperature coefficients of conductivity are exceptionally large, and the coefficients expressed in conductivity units increase with rise in temperature. The dissociation constants of dinitroaminophenol and naphthionic acid also increase slightly with dilution. Ostwald[1] has accounted for all of these facts by assuming that at low temperatures and high concentration these amino acids form inner salts, which break down on raising the temperature or the dilution, or both, yielding the free acid. This acid conducts better than the salt itself. In other words, conductivity rises exceptionally rapidly with temperature and dilution. Walker[1] has also advanced a theory accounting for the increase of the "constants" with dilution. Since our data do not exhibit this phenomenon to any striking degree, a lengthy discussion of his article here would be superfluous. Briefly, he says that these amino acids are amphoteric electrolytes, and have two dissociation constants, corresponding to dissociation into acid and base.

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[1] Z. physik. Chem., **3**, 261 (1889).

Probably the finest example of decreasing dissociation with rise in temperature is found in the case of dichloroacetic acid—a typical strong acid. This attains maximum dissociation at $V = 1024$ at the lower temperatures, and $V = 2048$ at the higher temperatures.

The increase, with dilution, in the "constants" of bromosuccinic acid may be accounted for by the fact that the second hydrogen ion probably begins to split off at higher dilutions, and the acid behaves as if it were dibasic. White and Jones observed a similar action in case of malonic, maleic, fumaric, succinic acids, etc.

Walden[2] has carried out a careful and elaborate set of experiments with substituted malonic acids, working at only one temperature, 25°. Our results agree with his. Arranging these acids in the order of their strengths we have:

Acid	$K \times 10^4$, 25°	$K \times 10^4$, 65°
Dimethylmalonic	7.45	7.01
Butylmalonic	10.8	9.4
Ethylmalonic	12.3	10.0
Isopropylmalonic	13.2	11.3
Benzylmalonic	15.5	12.0
Allylmalonic	16.0	13.4
Malonic[3]	16.3	....
Methylethylmalonic	16.5	14.6
Diethylmalonic	74.0	50.0
Dipropylmalonic	113.0	79.0

Walden's arrangement is precisely the same, except that he places malonic acid below methylethylmalonic. Our observations then agree with his—malonic acid is stronger than any of its monosubstituted products, and is weaker than any of the disubstituted acids, with the exception of dimethylmalonic acid. Temperature seems to have no influence on the relative strengths of the acids. There seems to be no rule governing the order in which the monosubstituted malonic acids fall. The strength of the disubstituted acids increases with increasing molecular weight, as Walden has pointed out. Combining his values and ours for disubstituted malonic acids:

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[1] Z. physik. Chem., **49**, 82 (1904).

[2] *Ibid.*, **8**, 433 (1891).

[3] Value found by Walden.

Acid	Molecular weight	$K \times 10^4$, 25°
Dimethylmalonic	132	7.45
Ethylmethylmalonic	146	16.5
Diethylmalonic	160	74.0
Diallylmalonic*	184	76.0
Dipropylmalonic	188	113.0
Benzylethylmalonic*	222	146.0
Dibenzylmalonic*	284	410.0

The asterisked acids were studied by Walden.

In this connection Ostwald[1] has calculated the conductivity of benzalmalonic acid from the formula $C_6H_5CH:C(COOH)_2$. We should scarcely know whether to call it a mono- or disubstituted acid. Both hydrogens of malonic acid are replaced, but by a single bivalent group. The behavior of this acid is equally perplexing. Its constant is 40.8—higher than that of any monosubstituted acid, but too low for the disubstitution table, where its place should be between dipropyl- and benzylethylmalonic acids, according to its molecular weight, 192.

The percentage temperature coefficients of these substituted malonic acids never decreased with increasing dilution. This decrease was observed by White and Jones[2] to be a general occurrence. In this we agree with the latter investigators.

Isomeric acids have long been the subject of experimental and theoretical investigation. Why do they behave differently? Are there no definite rules governing their action?

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[1] Z. physik. Chem., **3**, 369 (1889).

[2] This Journal, **44**, 198 (1910).

Ostwald,[1] Walker[2] and very recently Derick[3] have worked on the correlation of ionization and structure for such acids, and on the nature of different substituting groups.

The following relation seems to hold for a limited number of cases, which have presented themselves in this investigation:

In the case of isomeric acids containing two carboxyl groups, the acid with these groups in the "ortho" or the "cis" position is always the stronger. For example:

o-Phthalic, $K = 12.1$ *m*-Phthalic, $K = 2.87$

and again,

Maleic, $K = 154$ Fumaric, $K = 11.1$

The more hydrated an acid is in solution the less its conductivity, other things being equal. If, of two isomeric acids, the one readily forms an anhydride on coming out of solution, while the other retains the constituents of water, it seems fair to assume that the former, in solution, will be the less hydrated—and, therefore, show the greater molecular conductivity. When it comes to measuring the limiting conductivities (μ_∞) for these acids, the case is entirely different. The sodium salt of *o*-phthalic, or maleic, acid cannot form an anhydride. Therefore, in solution there is no reason why it should be less hydrated than its isomer. And since it actually shows the same molecular conductivity, it is probably hydrated to exactly the same extent. So, as has long been known, isomeric acids should have, and actually do have, the same μ_∞. The hydrated acid with a small molecular conductivity will give a smaller percentage dissociation when divided by μ_∞ than the unhydrated acid with the larger molecular conductivity, when divided by the same μ_∞. Therefore, its constant will be smaller, or, as we say, the acid will be weaker.

In the case of amino acids the proximity of the substituting groups might be expected to facilitate the formation of inner salts. In this connection we have compared results obtained for metanilic and sulphanilic acids, also for *o*- and *p*-aminobenzoic acids. In each case the acid with neighboring groups gives more evidence of inner salt formation than does its isomer. Under the discussion of the amino acids, we enumerated some of the characteristics due to this inner salt formation. The percentage temperature coefficients were exceptionally large; the temperature coefficients expressed in conductivity units increased with rise in temperature; the percentage dissociation increased with rise in temperature. By comparing the following data it will be seen that metanilic acid exhibits these characteristics in a more striking degree than does sulphanilic acid:

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[1] Z. physik. Chem., **3**, 170 (1889).

[2] J. Chem. Soc., **61**, 605 (1892); **67**, 147 (1895).

[4] J. Am. Chem. Soc., **33**, 1881 (1911); **34**, 74 (1912).

Percentage Temperature Coefficients

V = 32	35°–50°	50°–65°
Metanilic acid	2.66	2.23
Sulphanilic acid	2.28	1.89

Temperature Coefficients (Cond. Units)

V = 1024	35°–50°	50°–65°
Metanilic acid	3.45	3.82
Sulphanilic acid	4.36	4.37

Dissociatiom Constants

	0°	65°	Per cent. increase
Metanilic acid	0.90	5.33	600
Sulphanilic acid	3.28	13.4	400

Moreover, metanilic acid conducts less than sulphanilic acid; and inner salts have lower conductivity than the acids from which they are formed. This seems sufficient evidence that *m*-amino acids have greater salt-forming power than the *p*-amino acids.

By a similar comparison of the data of White and Jones[1] on *o*- and *p*-aminobenzoic acids, it will be seen that the para acid again forms less of the inner salt than does its isomer.

In the introduction of this article we stated that we would compare a few conductivity measurements made with the same acid by different investigators. Because of disagreements in the results obtained by our predecessors, we repeated the measurements for the following acids at higher temperatures.

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[1] This Journal, **44**, 195–6 (1910).

Salicylic Acid, 35°. Molecular Conductivity

V	White and Jones[1]	Clover and Jones[2]	Springer
64	92.80	94.27	93.64
128	125.1	126.1	126.0
512	207.0	210.3	209.7
1024	255.4	253.3	255.0
2048	295.7	294.5	294.6

In this case our results appear to be about the mean between the results of White and Jones and those of Clover and Jones. The agreement in the results obtained with the following acid is more satisfactory:

o-Phthalic Acid, 35°. Molecular Conductivity

V	White and Jones	Clover and Jones	Springer
64	98.48	96.20	96.31
128	128.9	128.2	128.06
512	212.5	213.3	212.8
1024	259.7	258.6	258.5
2048	306.0	301.9	302.7

We have also had the opportunity of repeating measurements made by earlier investigators, and comparing our results:

Ethylmalonic Acid, 25°. Molecular Conductivity

V	Ostwald[3]	Walden[4]	Springer
32	64.5	65.07	64.42
128	115.0	117.6	114.55
512	188.0	192.0	188.9
1024	229.0	236.0	231.2

These are what we might call our average agreements. There are, of course, cases in which the difficulties are greater—and acid such as acetylsalicylic, which hydrolyzes and decomposes.

Acetylsalicylic Acid, 25°. Molecular Conductivity

V	Ostwald[5]	Springer
128	65.7	60.6
512	117.2	109.3
1024	151.5	139.3

Such a case as this, however, is really exceptional.

[1] THIS JOURNAL, **44**, 189 (1910).

[2] *Ibid.*, **43**, 213 (1910).

[3] Z. physik. Chem., **3**, 284 (1889).

[4] *Ibid.*, **8**, 449 (1891).

[5] *Ibid.*, **3**, 264 (1889).

SUMMARY

Most of the facts established by White and Jones[1] and by Wightman and Jones[2] have been confirmed by the present work. Some of the more obvious of these relations have not been discussed in detail, since reference to our data will suffice to show that they hold.

1. The percentage temperature coefficients of conductivity of the organic acids are generally small, and of the same order of magnitude, and decrease with rise in temperature.

2. The temperature coefficients, expressed in conductivity units, increase rapidly with dilution and decrease with rise in temperature. The stronger the organic acid, the larger these conductivity units.

3. The percentage temperature coefficients of the amino acids are exceptionally large, and the coefficients expressed in conductivity units increase with rise in temperature. The internal salt-forming power of these amphoteric electrolytes explains this behavior.

4. The conductivity of most organic acids is a parabolic function of the temperature, as has been pointed out by Euler[3]. This may be seen by comparing observed values with those calculated from the formula

$$\lambda = a + bt - ct^2$$

5. Change in temperature does not seem to influence the relative strengths of organic acids.

6. Strong organic acids do not obey the Ostwald dilution law.

7. Most dibasic organic acids dissociate like monobasic acids.

8. The migration velocities of the anions of organic acids are a function of the number of atoms present in the anions, and μ_∞ values for dibasic acids may be found by means of this principle.

9. The relation of dissociation of organic acids to temperature seems to be irregular. In general, the maximum disso-

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[1] This Journal, **44**, 198 (1910).

[2] *Ibid.*, **46**, 111 (1911).

[3] Z. physik. Chem., **21**, 257 (1896).

ciation has been reached at the temperatures worked with. The dissociation of only the amino acids increases at temperatures higher than 50°.

10. Isomeric acids do not behave similarly as regards change in their dissociation.

11. A relation has been found which possibly connects the behavior of some isomeric acids with their structure and power to form inner salts and anhydrides.

CHEMICAL LABORATORY
JOHNS HOPKINS UNIV.
May, 1912

SOLUBILITY AND DISTRIBUTION COEFFICIENTS OF THYMOL[1]

BY ATHERTON SEIDELL

According to the theory of alcohol narcosis developed by Meyer and Overton, the activity of a given narcotic is proportional to its coefficient of distribution between the blood and the fatty substance of the animal cells. Since it was impracticable to use these two solvents for the experimental determination of the coefficients of distribution, the problem was simplified by using water in place of the blood and olive oil as the representative of the fatty substance of the cells. This oil appears to have been chosen arbitrarily and no data are given to show that it most nearly represents the oil of the body-cells, or whether other oils would give sufficiently varying distribution coefficients to alter the observed parallelism between the narcotic action and the distribution coefficient. Experiments along this line were probably not considered necessary in the case of the narcosis theory on account of the more or less uncertainty of the observed values for the physiological activity. Furthermore, the better known plant and animal oils are composed in general of similar constituents and have fairly closely agreeing physical properties, therefore it may be supposed that the solubility of a given compound in a number of different oils would not vary significantly, and consequently the distribution coefficients would agree fairly satisfactorily. There are, however, so far as I have been able to ascertain, no published data on this point and consequently no estimate of the magnitude of the possible variations obtained with different oils can be made.

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[1] Presented at the 8th International Congress of Applied Chemistry, New York, Sept., 1912.

The opportunity to make some experiments along this line presented itself in connection with studies which are now being made in this laboratory upon thymol, a drug which is used very extensively in the treatment of hook-worm disease. This drug has been found to be superior to all other vermifuges which have so far been tried, but its use is attended with certain dangers and there is need for a safer and more efficient remedy for combatting the hook-worm. It was therefore thought that solubility and distribution studies upon thymol would serve to answer the point just raised in connection with the narcosis theory and also assist in an understanding of the manner in which thymol exerts its action in the organism.

In connection with the question as to the physiological action of thymol, it might at first be supposed that its power of dislodging the worms from the alimentary tract is due to its irritating properties, that is, that it acts mechanically and passes out of the body more or less unchanged. Against this view, however, is the fact that β-naphthol, which also has considerable effect upon hook-worms, has comparatively little volatility. Furthermore, experiments which will be described in another paper from this laboratory show that none or only a very small proportion of the administered thymol comes through the alimentary tract as such.

The solubility and distribution experiments described in the following pages were all made with the aid of a gas-heated water bath maintained at constant temperature (within ±0°.05) by means of a toluene regulator. The cork-stoppered glass vessels containing the solutions were attached to a rotating frame by the aid of which gentle agitation of the solutions was secured for periods of 18 hours or longer in all cases.

The determination of the dissolved thymol was made by the recently developed bromine-hydrobromic acid method.[1]

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[1] Seidell: This Journal, **47**, 520 (1912).

In the case of the determinations of the solubility in oils the weighed saturated solution was subjected to steam distillation and the first three distillates of about 150 cc. each were separately titrated in all cases. The complete removal of the dissolved thymol was thus assured.

The sample of thymol was the same as used for the experiments upon the bromine-hydrobromic acid method and analytical results there shown are the evidence of its degree of purity.

Although the distribution experiments were made first, the results will not be given until after the solubility determinations are described. This appears the better plan since the distribution ratios are also the ratios of the solubilities in the two solvents, and on this basis distribution coefficients in addition to those directly determined may be calculated from the solubility results.

The Solubility of Thymol in Water at Different Temperatures.—In all of the determinations an excess of thymol was rotated with about 110 cc. of water for 18 hours or longer, and 100 cc. of the clear aqueous solution were withdrawn and titrated by the bromine-hydrobromic acid method. The result at 37° is the average of five determinations. The specific gravity of the saturated solution at this temperature was found to be $d_{37}^{37} = 1.000$.

Experimental determinations		Interpolated values read from curve	
$t°$	Grams thymol per 100 grams sat. solution	$t°$	Grams thymol per 100 grams sat. solution
13	0.0737	10	0.067
15	0.0754	15	0.077
22	0.0936	20	0.088
25	0.0981	25	0.0995
29.5	0.1104	30	0.112
37.0	0.1320	35	0.126
		37	0.132
		40	0.141

A single determination reported by Zdarek[1] gives the value 0.0948 gram thymol per 100 cc. saturated solution at 19°.4.

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[1] Z. anal. Chem., **41**, 227–231 (1902).

This result is about 16 per cent. too high as compared with the above values; the difference is easily explained by the fact that the Koppeschaar bromate method was used by Zdarek for the titration of the thymol and this method, as shown by my results,[1] gives high and variable results.

The Solubility of Thymol in Aqueous Hydrochloric Acid Solutions at 25°.—A series of solutions of hydrochloric acid of concentrations varying from 0.1 to 5.0 normal were prepared and an excess of thymol was added to about 150 cc. portions of each of these and the mixtures rotated at 25° for approximately 40 hours. Since preliminary experiments had shown that thymol could not be accurately determined in acid solutions brought to neutrality to phenolphthalein by the addition of caustic alkali, it was found necessary to resort to a method of steam distillation of the neutralized saturated solutions. The 100 cc. portion of the solution was therefore placed in a distilling flask of about 600 cc. capacity, 2 drops of phenolphthalein added, and fairly concentrated alkali slowly dropped in until a distinct pink color was imparted to the solution. The flask was then connected with a condenser and the distillation with a current of steam continued until three distillates of about 150 cc. each were obtained. These were each titrated by the bromine-hydrobromic acid method and the amount of dissolved thymol calculated from the used thiosulphate. The detailed results are given in the accompanying table (No. I).

The results, when plotted on cross-section paper, yield a perfectly regular curve. One determination was made at 37°.2, and this result serves as a check upon the 25° values, since the corresponding exterpolated value for the 5.0 N hydrochloric acid at 25° differs from the 37°.2 result by the same amount that was found for the difference of the solubility in water at 25° and 37°.2. Therefore a curve drawn parallel to the 25° results beginning at the figure for the solubility in water at 37°.2 and ending at the solubility in 5.0 N hydrochloric acid at the same temperature gives a close approximation to the solubility of thymol in aqueous hydrochloric

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[1] *Loc. cit.*

Table I.–Solubility of Thymol in Aqueous Hydrochloric Acid Solutions at 25°

Det. No.	Solvent	d_{25}^{25} of the sat. solution	Vol. of sat. sol. used for distillation cc.	Distillate No.	cc. thiosulphate for		Diff.	Calc. grams thymol per 100 cc. sat. solution
					Br	HBr		
1	0.1 N HCl	1.002	100	1	20.7	47.2	26.5	0.09677
				2	13.9	14.8	0.9	
				3	12.25	12.6	0.35	
2	0.5 N HCl	1.009	100	1	18.7	41.85	23.15	0.08839
				2	14.85	16.75	1.9	
				3	7.7	8.0	0.3	
3	1.0 N HCl	1.018	100	1	28.35	48.4	20.05	0.08019
				2	13.6	16.1	2.5	
				3	11.4	11.85	0.45	
4	2.5 N HCl	1.043	100	1	21.15	27.85	16.7	0.06117
				2	10.5	11.05	0.55	
				3	10.0	10.3	0.3	
5	5.0 N HCl	Dissolved thymol estimated by exterpolation = 0.0445						
5(*a*)[1]	5.0 N HCl	1.081	45.16	1	37.0	45.6	8.6	0.0772
				2	16.5	17.8	1.3	

[1] This solution saturated at 37°.2. Factor for standard thiosulphate; readings × 0.9295 = 0.05 N exactly. In the case of determination No. 5(*a*) the factor was: readings × 0.9384 = 0.05 N exactly.

acid solution at 37°.2. The values read from such a curve as compared with those actually determined at 25° are as follows:

Concentration of HCl	Gram thymol per 100 cc. sat. solution at 25°	37°.2
0.0	0.0995	0.132
0.1 N	0.0968	0.129
0.5 N	0.0884	0.121
1.0 N	0.0802	0.112
2.5 N	0.0612	0.0935
5.0 N	0.0445	0.0772

These results show that with increasing concentration of hydrochloric acid there is a regular decrease in the amount of dissolved thymol. Since the free acidity of the gastric juice of man is equivalent to approximately 0.2 per cent. hydrochloric acid, or 0.055 normal, and that of the dog is 2.7 per cent., or approximately 0.74 normal, it will be seen from the above values at 37°.2 that the diminution of the solubility of thymol in the gastric juice of man amounts to 100—0.1305/0.132 = 1.2 per cent. and the decrease in the gastric juice of the dog amounts to 100—0.1165/0.132 = 11.7 per cent.

Solubility of Thymol in Olive Oil at Temperatures between 10° and 40°.—The olive oil which was used for all of the solubility and distribution experiments was a portion of an imported sample which had been analyzed at the Bureau of Chemistry and found to be genuine and free from other oils which might be present as adulterants. The saturated solutions were prepared by rotating the oil with a sufficient excess of thymol for the periods of time shown in the accompanying table (No. II). The specific gravities were determined by means of a 10 cc. pycnometer. It was found that irregular values for the dissolved thymol were obtained if the weighed sample to be used for the steam distillation was introduced in the distilling flask in the narrow weighing bottle in which it had been weighed or even in a porcelain combustion boat. The trouble appeared to be that the oil formed globules on the inner walls of the bottle or weighing boat and these globules were not dislodged by the current of steam. The difficulty was entirely overcome by weighing the sample from a short glass tube provided with a stopcock on the lower end. By means of this miniature burette the desired amount of the saturated solution was dropped directly into the distilling flask and its weight determined by difference. About 150 cc. of water were added and the steam distillation continued until three distillates of about 150 cc. each were obtained. These were separately titrated by the bromine-hydrobromic acid method and the dissolved thymol calculated from the sum of the thiosulphate consumed in the three titrations.

The results are shown in Table II, calculated to both the weight and volume basis of expressing the concentrations of dissolved thymol.

Table II.—Solubility of Thymol in Olive Oil at Various Temperatures

Experimental Determinations

No.	Rotation period Hrs.	$t°$	Sp. gr.[1] of saturated solution	Grams thymol per 100 grams sat. solution
1	18	13.0	0.9373	32.7
2	20	15.3	0.9370	33.5
3	18	22.0	0.9369	36.7
4	36	25.0	0.9374	40.0
5	52	29.5	0.9387	45.3
6[2]	20–60	37.3	0.9438	55.9

Interpolated Values

	Specific gravity of the		Grams thymol per 100 grams		Grams thymol per 100 cc.	
$t°$	Solvent	Sat. solution	Olive oil	Sat. solution	Olive oil	Sat. solution
10	0.9188	0.9376	46.2	31.6	42.4	29.6
15	0.9168	0.9370	50.1	33.4	46.0	31.3
20	0.9150	0.9368	56.2	36.0	51.5	33.7
25	0.9132	0.9373	66.9	40.1	61.1	37.6
30	0.9116	0.9389	84.5	45.8	77.0	43.0
35	0.9100	0.9418	111.0	52.6	101.1	49.6
37	0.9093	0.9435	124.3	55.4	112.9	52.3
40	0.9083	0.9463	151.9	60.3	137.9	57.1

[1] The specific gravities are calculated in all cases on the basis of the weight of a unit volume of water at the temperature of the experiment.

[2] Average of three determinations.

The Solubility of Thymol in Other Oils.—The method used for determining the solubilities in the several other oils was exactly the same as described above for olive oil. The results are combined in Tables III and IV and all of the curves shown in the accompanying diagram:

Table III.—Solubility of Thymol in Several Oils

Experimental Determinations

	In peanut oil		In cod liver oil		In liquid petroleum	
t°	Sp. gr. of sat. solution	Grams thymol per 100 grams sat. solution	Sp. gr. of sat. solution	Grams thymol per 100 grams sat. solution	Sp. gr. of sat. solution	Grams thymol per 100 grams sat. solution
15.3	....	....	0.945	34.6	0.8798	3.90
22.0	0.9409	42.7	0.943	35.9	0.8807	5.99
29.5	0.9392	44.9	0.9434	42.9	0.8822	13.41
37.2	0.9425	56.8	0.946	53.9	0.8886	23.32

Interpolated Values

	In peanut oil		In cod liver oil		In liquid petroleum	
t°	Sp. gr. of sat. solution	Grams thymol per 100 grams of peanut oil	Sp. gr. of sat. solution	Grams thymol per 100 grams cod liver oil	Sp. gr. of sat. solution	Grams thymol per 100 grams liquid petrolatum
10	0.9470	73.0	0.9480	50.0	0.8795	3.1
15	0.9440	73.8	0.9450	52.0	0.8798	3.95
20	0.9417	74.6	0.9435	55.5	0.8802	5.6
25	0.9399	76.4	0.9430	63.1	0.8808	9.78
30	0.9392	83.2	0.9435	77.0	0.8824	16.3
35	0.9410	106.7	0.9450	102.0	0.8860	25.5
37	0.9425	130.5	0.9460	116.5	0.8884	29.9
40	0.9450	212.5	0.9478	150.0	0.8944	38.9

Table IV.—Solubility of Thymol in Several Oils

Experimental Determinations

	In castor oil		In cottonseed oil		In linseed oil	
t°	Sp. gr. of sat. solution	Grams thymol per 100 grams sat. solution	Sp. gr. of sat. solution	Grams thymol per 100 grams sat. solution	Sp. gr. of sat. solution	Grams thymol per 100 grams sat. solution
15.3	....	...	0.943	39.12	...	....
22.0	0.9525	51.71	0.945	44.21	0.948	39.9
29.5	0.9660	57.31	0.946	52.31	0.948	43.3
37.2	0.9785	64.55	...	...	0.948	53.7

Interpolated Values

	In castor oil		In cottonseed oil		In linseed oil	
t°	Sp. gr. of sat. solution	Grams thymol per 100 grams castor oil	Sp. gr. of sat. solution	Grams thymol per 100 grams cottonseed oil	Sp. gr. of sat. solution	Grams thymol per 100 grams linseed oil
10	0.935	81.2	0.942	56.2	0.948	62.3
15	0.942	90.2	0.943	64.0	0.948	63.1
20	0.950	101.5	0.944	74.2	0.948	65.1
25	0.958	116.5	0.945	89.4	0.948	69.0
30	0.967	137.0	0.946	113.7	0.948	78.3
35	0.975	165.0	0.948	146.5	0.948	100.0
37	0.979	180.0	0.9485	166.5	0.948	116.5
40	0.984	213.0	0.949	217.5	0.948	152.0

The Distribution of Thymol between Water and Olive Oil.—According to the general plan of the experiments, weighed amounts of thymol were added to mixtures of accurately measured amounts of oil and water, usually 10 cc. of oil and 100 cc. of water. The tubes containing these mixtures were rotated at constant temperature for approximately two days in all cases. The amounts of thymol were chosen to give very wide differences in the concentrations of the solutions. After the period of rotation the vessels containing the mixtures were removed from the bath in a large beaker filled with the water of the bath. This was done in order that the aqueous layer could be withdrawn more easily. Since it was necessary to withdraw the lower aqueous layer without simultaneously removing any of the oil, a glass tube with its lower end closed with paraffin was first introduced and the siphon tube then inserted through this. After pushing away the lump of paraffin, the end of the siphon tube was well below the oil layer and little difficulty was experienced in withdrawing nearly all of the clear aqueous solution. After ascertaining the volume, its contained thymol was determined by the bromine-hydrobromic acid method of titration. From the data thus obtained the concentration of the oil layer was calculated by difference. The specific gravity of the oil layer was ascertained by means of a specific gravity table, showing the density of various mixtures of oil and thymol at several different temperatures. These values, as determined for olive, peanut and cod liver oils, are shown in Table V. They make pos-

Table V.—Specific Gravities of Solutions of Thymol in Olive Oil, Peanut Oil and Cod Liver Oil at Various Temperatures

(The specific gravities are calculated in all cases on the basis of the weight of unit volume of water at the temperature of the experiment)

Wt. per cent. thymol in mixture	Specific gravity of solution of thymol in											
	Olive oil at:				Peanut oil at:				Cod liver oil at:			
	13°	20°.6	29°.6	37°	13°	20°.6	29°.6	37°	13°	20°.6	29°.6	37°
0	0.9174	0.9147	0.9118	0.9093	0.9194	0.9166	0.9133	0.9109	0.9285	0.9252	0.9219	0.9198
5	0.9205	0.9177	0.9146	0.9122	0.9225	0.9195	0.9161	0.9137	0.9311	0.9277	0.9244	0.9221
10	0.9236	0.9207	0.9176	0.9151	0.9254	0.9224	0.9189	0.9165	0.9337	0.9303	0.9269	0.9246
15	0.9266	0.9238	0.9206	0.9181	0.9284	0.9252	0.9217	0.9193	0.9363	0.9329	0.9294	0.9270
20	0.9298	0.9269	0.9236	0.9211	0.9314	0.9281	0.9246	0.9222	0.9390	0.9355	0.9319	0.9295
25	0.9328	0.9300	0.9266	0.9240	0.9344	0.9310	0.9274	0.9250	0.9416	0.9381	0.9344	0.9320
30	0.9359	0.9330	0.9295	0.9270	0.9374	0.9340	0.9303	0.9278	0.9443	0.9407	0.9370	0.9344
35	0.9390	0.9361	0.9325	0.9300	0.9404	0.9368	0.9330	0.9306	0.9470	0.9433	0.9394	0.9368
40	0.9420	0.9393	0.9355	0.9330	0.9433	0.9397	0.9358	0.9334	0.9496	0.9459	0.9420	0.9393
45	0.9451	0.9423	0.9385	0.9360	0.9463	0.9426	0.9386	0.9362	0.9523	0.9484	0.9445	0.9416
50	0.9482	0.9453	0.9416	0.9390	0.9492	0.9455	0.9414	0.9390	0.9549	0.9510	0.9470	0.9441

The figures below the horizontal lines refer to supersaturated solutions.

sible the necessary calculation of the distribution results to the basis of volume concentration.

In addition to the results at 37°.2, Table VI, a series of determinations was also made at 25°. The amounts of olive oil used in the several mixtures were introduced from a weight burette instead of being measured from an ordinary burette as in all the other experiments. The calculation of the volumes of the olive oil layer was made by means of the specific gravity determinations shown in Table V. The following results were obtained (Table VII):

Table VI.—Distribution of Thymol between Water and Olive Oil at 37°.2

Composition of mixtures			Grams thymol found per 100 cc. aq. layer (C_w)	Grams thymol per 100 grams olive oil (calc. by diff.)	Grams thymol per 100 cc. olive oil layer (calc.) (C_o)	Dist. coefficient C_o/C_w
Cc. H_2O	Cc. olive oil	Grams thymol				
80	10	9.0	0.1087	97.38	46.35	427
100	10	8.0	0.1053	86.92	43.60	414
80	10	7.0	0.0987	76.12	40.67	412
80	10	6.0	0.0921	64.74	36.67	398
80	10	5.0	0.0807	55.54	33.48	415
100	10	4.0	0.0695	43.26	28.00	403
100	10	4.0	0.0682	42.96	27.93	410
100	10	2.0	0.0395	21.58	16.31	403
100	10	2.0	0.0381	21.44	16.24	426
100	10	1.0	0.0215	10.69	8.83	410
100	10	0.5	0.0122	5.37	4.64	382
100	10	0.5	0.0122	5.33	4.61	378
					Average	406

Ratio of the solubilities 52.3/0.132 = 397

Table VII.—Distribution of Thymol between Water and Olive Oil at 25°

Composition of mixtures			Gram thymol found per 100 cc. aq. layer (C_w)	Calc. grams thymol per 100 cc. oil layer C_o	C_o/C_w
Cc. H_2O.	Cc. olive oil	Grams thymol			
80	10	8.0	0.1014	44.95	443
100	10	6.0	0.0848	36.34	428
100	10	4.0	0.0655	29.43	450
100	10	2.0	0.0349	16.26	465
100	10	1.0	0.0185	8.80	474
100	10	0.5	0.0106	4.54	430
				Average	450
Ratio of the solubilities			(0.0995	37.6)	377

It will be noted that in the case of the first determination the amount of thymol in each layer is greater than the solubility at 25°, indicating, therefore, supersaturation. The distribution ratio is considerably higher than the ratio of the solubilities in oil and water. The difference is greater than can be explained on the basis of experimental error, and is probably due to an imperfect separation of the two layers. It was noted that the olive oil layers were not clear in all cases and, furthermore, that on titrating water which has been rotated with the oil, a consumption of bromine corresponding to about 1.0 cc. of 0.05 N thiosulphate per 100 cc. of the water occurred. A correction for this error would make the above observed difference in the coefficients even greater than shown.

The Distribution of Thymol between Water and Cod Liver Oil.—The determinations were made exactly as described for olive oil. In the case of the results at 37° the tubes were rotated for 2 days and allowed to stand 8 days before beginning the analysis of the aqueous layers. At 25° the time of rotation was 18 hours in the case of some and 36 hours in the case of the other tubes of the series.

Composition of mixtures			Gram thymol found per 100 cc. aq. layer (C_w)	Calc. grams thymol per 100 cc. cod liver oil layer (C_o)	C_o/C_w
Cc. H_2O	Cc. cod liver oil	Grams thymol			
Results at 37°:					
80	10	8.0	0.1099	43.81	399
80	10	5.0	0.0862	32.90	380
100	10	3.0	0.0574	22.51	392
100	10	1.0	0.0250	8.86	357
				Average	382
Ratio of solubilities			(0.132	53.3)	404
Results at 25°:					
100	10	9.0	0.1079	49.00	454
134	10	5.0	0.0816	32.58	400
160	10	2.0	0.0371	16.18	436
160	10	0.5	0.0127	4.57	359[1]
				Average	423
Ratio of solubilities			(0.0995	40.7)	409

Distribution of Thymol between Water and Peanut Oil.—A series of determinations made at 25° with peanut oil gave the following results:

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[1] Omitted from average.

Composition of the mixture			Gram thymol found per 100 cc. aq. layer (C_w)	Calc. grams thymol per 100 cc. peanut oil layer (C_o)	C_o/C_w
Cc. H_2O	Cc. peanut oil	Grams thymol			
100	10	9.0	0.1077	46.48	431
130	10	5.0	0.0786	32.45	413
160	10	2.0	0.0395	16.16	409
160	10	0.5	0.0088(?)	4.63	523[1]
				Average	417
Ratio of solubilities			(0.0995	36.5)	367

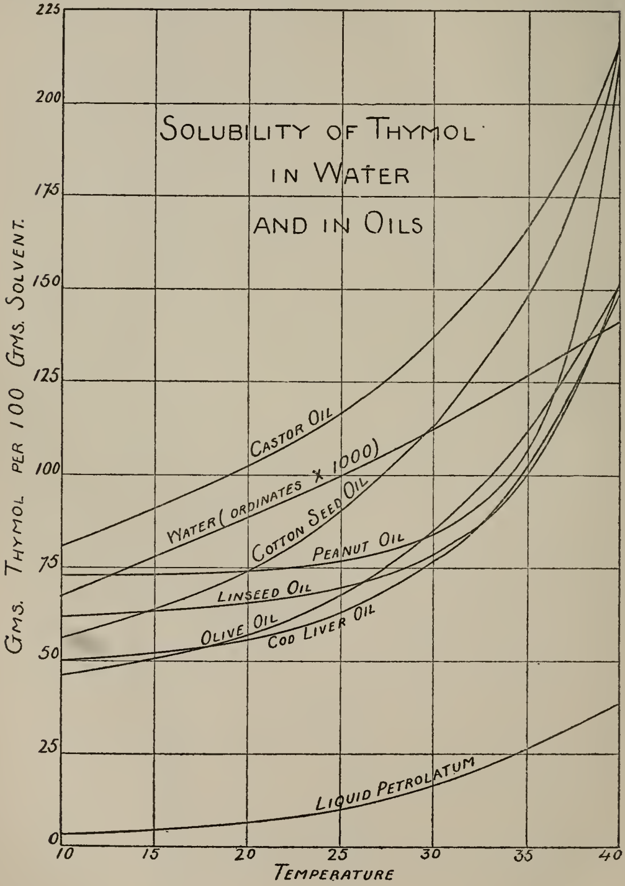
These determinations confirm those for olive oil and for cod liver oil made at 25° in that a higher distribution value is found than corresponds to the ratio of the solubilities of thymol in peanut oil and in water at this temperature. No satisfactory explanation of this difference is apparent, especially since at the higher temperature, 37°, the distribution coefficient was not found to be appreciably higher than the ratio of the solubilities. Although this difference at 25° has been found, it is apparent that both values for the coefficient cannot be correct. On account of the many analytical difficulties due particularly to the very great difference in the amounts of the thymol in the two layers and to the imperfect separation of the oil and water in some cases it would appear more rational to select, as the true distribution coefficients, the ratios of the solubilities in the two solvents. The values at 37° so obtained from the solubility results reported in the preceding tables, I to IV, inclusive, are as follows (Table VIII):

Table VIII.—Showing the Distribution Coefficients of Thymol between Water and Oils as Calculated from the Respective Solubilities at 37°.

Oil	Grams thymol per 100 cc. sat. solution in: Oil (C_o)	Water (C_w)	Dist. coefficient C_o/C_w	
Liquid petrolatum	20.4	0.132	155	
Cod liver oil	50.9	0.132	386	Average 393
Linseed oil	51.0	0.132	386	
Olive oil	52.3	0.132	397	
Peanut oil	53.3	0.132	404	
Cottonseed oil	59.3	0.132	449	
Castor oil	62.9	0.132	477	

[1] Omitted from average.

Excluding the liquid petrolatum, these results show that the distribution coefficient is practically the same for four of the oils and not very different for the other two.



An examination of the diagram representing the solubilities of thymol at different temperatures shows that at lower temperatures the differences in the calculated distribution coefficient would be much greater than at 37°. However, in studies of the distribution of drugs it is their conduct at body temperature, viz., 37°, which is of particular interest and it may therefore be concluded that for this purpose olive oil is fairly representative and its selection for distribution studies is justifiable.

HYGIENIC LABORATORY
WASHINGTON, D. C.
June, 1912

REVIEWS

EXPERIMENTS IN ORGANIC CHEMISTRY. A Laboratory Manual Designed to Accompany Outlines of Organic Chemistry. By F. J. MOORE, PH.D., Associate Professor of Organic Chemistry in the Massachusetts Institute of Technology. New York: John Wiley & Sons; London: Chapman & Hall, Limited. 1911. pp. vi + 29. Price, $0.50.

This laboratory manual was prepared to be used with Prof. Moore's Outlines of Organic Chemistry in a brief course for engineering students. The experiments are therefore simple preparations that can be made in 15 laboratory periods of 3 hours each. The exercises embrace tests for nitrogen, halogens and sulphur, and the study of about 30 typical substances such as ethyl alcohol, ethyl bromide, formic acid, acetic acid, acetyl chloride, acetic anhydride, ethyl acetate, acetaldehyde and such substances.

The directions are clear and the questions make the students think. The experiment in which milk is separated into water, fat, casein and milk sugar is worthy of note. The book is a splendid one for the purpose. S. F. ACREE

TABLES ANNUELLES INTERNATIONALES DE CONSTANTES ET DONNÉES NUMÉRIQUES DE CHIMIE, DE PHYSIQUE, ET DE TECHNOLOGIE. Volume I. Année 1910. Publiées sous le patronage de l'Association international des Académies par le Comité international nommé par le VII Congrès de Chimie appliquée (Londres, juin, 1909). Paris: Gauthier-Villars; Chicago: University of Chicago Press. 1912. pp. xxx + 727. Price, bound, $6 ($6.54, postage prepaid); unbound, $5.30 ($5.82, postage prepaid).

The enormous increase in our chemical literature makes it impossible for an active investigator, or indeed anyone, to keep pace with even the few subjects in which he is interested. We must rely more and more upon the compilations of references from the literature, such as Beilstein's Handbuch der organischen Chemie, Abegg's Handbuch der anorganischen Chemie, and the Physikalisch-chemische Tabellen by Landolt-Boernstein-Meyerhoeffer. It is certainly better for long established societies to finance and produce such volumes, and the first Tables Annuelles mark the beginning of a movement which must end in the publication and distribution of all references to chemical and physical literature and biography by an International Society.

The Table of Contents of this volume includes about 45 subjects, such as density, viscosity, radiation, electricity, atomic weights, reaction velocities, solubilities, optical rotation, conductivities, electromotive forces and mechanical constants. The names of the International Committee and of the collaborators give assurance that the data and constants published are thoroughly trustworthy, and that the best method of arrangement of the material will soon be found. The committee promises to publish the volume for 1911 before the end of 1912.

The reviewer fears that the paper and binding are too poor to withstand the wear and tear which such an important volume will receive. S. F. ACREE

THE ANALYST'S LABORATORY COMPANION. A Collection of Tables and Data for the Use of Public and General Analysts, Agricultural, Brewers' and Works' Chemists, and Students, together with Numerous Examples of Chemical Calculations and Concise Descriptions of Several Analytical Processes. By ALFRED E. JOHNSON, B.Sc., Lond., F.I.C., A.R.C.Sc.I. Fourth Edition, Thoroughly Revised, with Additions. Philadelphia: P. Blakiston's Son & Co. 1912. pp. ix + 164. Price, $2.00.

This book, as its descriptive title suggests, contains a great deal of information and at least some of its data will be valuable to any busy chemist. The book has been carefully prepared and is printed in a handy form. It is written, however, from a British standpoint and considerable space is devoted to legal requirements and to analytical methods which do not apply to conditions in the United States and the fact is not noted that our system of weights and measures does not correspond exactly to the system used in Great Britain. For example, the U. S. gallon is not quite equal to 4 metric liters, whereas the only gallon mentioned is given as equal to 4.54596 liters. The author does not fully appreciate the proper use of significant figures. Thus, values hardly accurate to one-tenth of one per cent. are, in some cases, given to as many as eight significant figures and seven-place logarithms are used when four places would be perfectly adequate.

WILLIAM T. HALL

An Introduction to Quantitative Analysis. By S. J. M. Auld, D.Sc. (Lond.), Ph.D., F.I.C., F.C.S., Head of the Chemical Department, South-Eastern Agricultural College (University of London), Wye, Kent. London: Methuen & Co., Ltd. 1912. pp. x + 215. Price, 5 s.

The author aims to provide an introductory course suitable for college and university students which shall avoid the details of special technical analysis; and he presents the course essentially without reference to underlying theoretical considerations, except in the case of indicators for acidimetry. A general introduction (Part I) is followed by the usual course of volumetric analysis, including a chapter on gas analysis (Part II), and that by gravimetric analysis (Part III). Some typical separations and procedures for the analysis of a few representative minerals constitute Part IV, and Part V deals with vapor density determinations and some experimental work on the determination of equivalent and combining weights. The appendix includes a series of useful tables.

The subject matter is, in general, that common to many books of the same scope and purpose, and the procedures chosen are those recognized as reliable. Most of the directions are carefully and thoughtfully prepared, but the author is surely inconsistent in employing such small quantities of material for analysis as to require less than 25 cc. of the standard volumetric solutions for titrations, and in rounding out many atomic weights to whole units, while at the same time he gives his factors to five places of decimals and uses five-place logarithms. Taken as a whole, however, the book is to be commended, although it seems to lack distinctive features of its own.

The publishers would have done well to omit the insertion of their book catalogue.

H. P. Talbot

Methods for Sugar Analysis and Allied Determinations. By Arthur Given, B.S., Chemist for the Cuban Sugar Refining Co. With 8 illustrations. Philadelphia: P. Blakiston's Son & Co. 1912. pp. xi + 75. Price, $2.00.

The work is a very valuable compendium, covering a wide range of subjects in this field. The subject matter is succinctly treated, yet sufficient details are given to make certain the proper method of procedure. The book has been written and arranged for the analyst rather than the investigator, and is particularly adapted to the needs of young chemists who are well grounded in the fundamentals, yet new to the subject. As Assistant Chemist in the Bureau of Chemistry, U. S. Department of Agriculture, the author had an excellent opportunity to make a comparative study of the numerous methods followed by different workers in this field. As a result, he has presented in most cases but a single method of analysis for each substance, and that method as a rule represents the best practice. Fairly complete references are given to more extended treatises, and about thirty pages have been devoted to standard tables. The entire work has been divided into 118 numbered parts, the numbers serving to identify the divisions throughout the work, thereby making for condensation and easy references. In common with most writers on this subject, the author has neglected to state the limitations of the methods given. The binding, printing, paper, etc., are excellent. FREDERICK BATES

KOLLOIDCHEMIE. Ein Lehrbuch von RICHARD ZSIGMONDY, Professor an der Universität Göttingen, Direktor des Instituts für anorganische Chemie. Mit 37 Figuren im Text. (Chemische Technologie in Einzeldarstellungen, herausgegeben von PROF. DR. FERDINAND FISCHER.) Leipzig: Verlag von Otto Spamer. 1912. s. xi + 294. Preis: geh., M. 15; geb., M. 17.

This contains a brief (pp. 1–85) introduction and elementary discussion of the properties and chief characteristics of colloids, their classification, and the theory of peptization, followed by a special part giving in considerable detail the preparation and properties of colloidal metals, nonmetals, oxides, sulphides, inorganic and organic salts, dyes, albumin, gelatin, hemoglobin and casein. The author explains in the preface that the difficulty of correctly generalizing so new and broad a field as colloid chemistry has led him to make the general discussion rather brief and of limited scope, and to bring out in the descriptions of the individual colloids the properties which have been discovered through the study of that particular material. The book follows this scheme conscientiously, giving quite complete descriptions of the work on individual colloidal materials, and in this respect is most satisfactory, but in the general discussion one feels that much has been sacrificed for the cause of brevity. The book is a valuable addition to the literature of colloid chemistry, is in no wise a duplicate of such books as Ostwald's or Freundlich's, and will serve perhaps as a basis for the more theoretical treatment of those authors. H. ISHAM

CHEMICAL WORKS. Their Design, Erection and Equipment. By S. S. DYSON and S. S. CLARKSON. London: Scott, Greenwood & Son; New York: D. Van Nostrand & Co. 1912. pp. xii + 207. Price, $7.50.

This book, divided into 11 chapters dealing with the design and equipment of chemical works, is of considerable interest.

The following subjects are considered: Choice of site, materials of construction and the general layout of works, the power plant, sulphuric, nitric and hydrochloric acid plants, sulphate of ammonia, artificial manure and high explosive plants, apparatus used in chemical plants, and appendix matter touching on the chemical engineer, the English Alkali Works Regulation Act, and welfare work or "Prosperity Sharing."

The most valuable part of the book is to be found in the description of plants for the manufacture of acids and other heavy chemicals enumerated. Scale drawings are given, and these are accompanied by descriptive matter, hints, etc., which give some valuable information. It would seem better to have had a set of specifications to accompany the drawings instead of giving the details in a more or less rambling description.

The contact process for the manufacture of sulphuric acid is only referred to in a few words as being inapplicable to England.

The recent improvements in the manufacture of this acid by the Chamber process are mentioned, but not embodied in the plan of the works as given by the authors.

The matter presented in the choice of site is a statement of common sense facts as to location, transportation facilities, etc., which might be presupposed in anyone who contemplated the erection of a chemical plant. Under "Power Plant" we find information which appears in any good book on mechanical engineering, a great part of the space being devoted to a description of the Parson steam turbine.

The authors point out the fact that electricity is being used more and more in chemical works, but the subject is not otherwise touched upon.

Considerable stress is laid on apparatus for fire prevention, but automatic sprinklers are not mentioned.

Under the head of "General Plant" is given a description of apparatus used in chemical plants such as centrifugals, filter presses, acid lifts, etc., which may be found in most up-to-date books on chemical engineering or the catalogues furnished by the manufacturers. An exception, however, appears in reference to the use of apparatus constructed of fused silica, which finds many applications in the manufacture of acids and is well described here.

The appendix matter is concerned with the English act regulating the manufacture of heavy chemicals and welfare work.

It is doubtful whether these subjects will be of much value to the chemical engineer in this country.

We believe that the new matter presented in this book is comparatively small and the price charged for the publication will prevent many from making use of it. SAMUEL A. TUCKER

DAS ERDÖL, SEINE PHYSIK, CHEMIE, GEOLOGIE, TECHNOLOGIE UND SEIN WIRTSCHAFTSBETRIEB. In fünf Bänden. Unter Mitwirkung von DRS. AISINMAN, ALBRECHT, GOULESCHAMBAROFF, HOLDE, HOLOBEK, KAET, LOSSEN, KOETTNITZ, SINGER, UBBELOHDE, WISCHIN und WOLFF, herausgegeben von C. ENGLER, o. ö. Professor an der Techn. Hochschule zu Karlsruhe, und H. VON HÖFER, o. ö. Professor an der Montanistischen Hochschule zu Leoben. I. Band, Erste Abteilung. Die Chemie und Physik des Erdöls, bearbeitet von C. ENGLER. Leipzig: Verlag von S. Hirzel. 1912. pp. xiv + 593. Price, M. 28.

This is the most recent, most exhaustive and most authoritative treatment of this subject that has appeared. Nothing apparently has been omitted, nor it is strange when one considers the authors, Profs. Engler and von Höfer. It should be readily accessible to all those who wish to know the subject of petroleum thoroughly. A. H. GILL

VOL. XLVIII DECEMBER, 1912 No. 6

AMERICAN

CHEMICAL JOURNAL

[Contributions from the Chemical Laboratory of Cornell University]

OCTOCHLOROINDIGO AND SOME DERIVATIVES OF TETRACHLOROANTHRANILIC AND TETRACHLOROPHTHALIC ACIDS

BY W. R. ORNDORFF AND E. H. NICHOLS

Tetrachloroanthranilic Acid

Tetrachloroanthranilic acid was first made by Tust,[1] who converted tetrachlorophthalic acid into tetrachlorobenzoic acid, nitrated this and then reduced the nitro compound. A much better method for making this acid is the one given by Graebe and Rostovzeff.[2] These authors found, while making an investigation of Hofmann's reaction, that tetrachlorophthalimide could be converted into tetrachloroanthranilic acid practically quantitatively by means of sodium hypochlorite in alkaline solution. Hofmann's reaction was again used by Villiger and Blangey,[3] who worked out the details of the most convenient method for the preparation of tetrachloroanthranilic acid that we have at present. They made the ammonium salt of tetrachlorophthalamic acid by dissolving tetrachlorophthalic anhydride in aqueous ammonia, precipitating the free tetrachlorophthalamic acid by adding a mineral acid and converting this into tetrachloroanthranilic acid by means of sodium hypochlorite in alkaline solution.

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[1] Ber. d. chem. Ges., **20**, 2441 (1887); **21**, 1533 (1888).

[2] *Ibid.*, **35**, 2748 (1902).

[3] *Ibid.*, **42**, 3550 (1909).

The directions of Villiger and Blangey were followed in making the crude tetrachloroanthranilic acid used in this investigation. Pure tetrachlorophthalic anhydride and a standardized alkaline hypochlorite solution are required. The pure tetrachlorophthalic acid used was obtained from the commercial product by the method described by Delbridge[1] and converted into the anhydride by heating for several days at 105°. The purity of this anhydride was checked by making determinations of its molecular weight.[2] A weighed portion of the anhydride was dissolved in tenth normal sodium hydroxide, using ten per cent. excess. On heating, solution took place rapidly and was complete after a few minutes' boiling. A few drops of a solution of phenoltetrachlorophthalein were added as the indicator and about 0.5 cc. excess of tenth normal hydrochloric acid. The solution was then boiled to expel carbon dioxide, cooled, and the excess of hydrochloric acid titrated with sodium hydroxide.

Substance Gram	Tenth normal sodium hydroxide cc.	Molecular weight
0.2808	19.63	286.1
0.3152	22.04	286.0
	Calculated for $C_8O_3Cl_4$,	285.8

The alkaline hypochlorite solution should contain two molecules of sodium hydroxide to one molecule of sodium hypochlorite. In the preparation of this solution, chlorine is passed into a ten per cent. solution of sodium hydroxide as rapidly as complete absorption will allow. The solution is kept at a temperature of about 5° by means of a freezing mixture and is stirred mechanically. Chlorine is run in until the proportion of sodium hypochlorite to sodium hydroxide is greater than one molecule of the former to two of the latter, assuming that all the chlorine reacts according to the equation

$$2Cl + 2NaOH = NaOCl + NaCl + H_2O.$$

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[1] This Journal, **41**, 414 (1909).

[2] International atomic weights for 1912 were used in all calculations.

The amount of chlorine added is checked by weighing from time to time.

The free sodium hydroxide in this solution is determined by titration with standard hydrochloric acid. The indicator is not added until the end point is nearly reached in order to avoid as much as possible the action of the hypochlorous acid on it. Tetraiodophenoltetrachlorophthalein was found to give a fairly sharp end point.

The sodium hypochlorite is determined by titration of the iodine liberated from potassium iodide by the hypochlorite in acetic acid solution. One molecule of sodium hypochlorite liberates two atoms of iodine. The iodine is titrated with a standard solution of sodium thiosulphate with an arrowroot starch solution as the indicator.

Sufficient sodium hydroxide is then added to the solution so that it contains two molecules of sodium hydroxide to one of the hypochlorite. This solution may be kept for some little time without undergoing much change.[1]

For the preparation of tetrachloroanthranilic acid according to the method of Villiger and Blangey, 286 grams of the pure, finely pulverized tetrachlorophthalic anhydride is dissolved in 400 cc. of twenty per cent. ammonium hydroxide and the solution poured at once into an excess of dilute sulphuric acid, kept cold by ice. The precipitated tetrachlorophthalamic acid is filtered off as rapidly as possible on a Buchner funnel with suction and washed with water. The moist acid is then dissolved at once in the requisite amount of sodium hydroxide contained in two liters of water and kept cold by ice. It was found that a rapid solution of the tetrachlorophthalamic acid could be effected if it was beaten up in 1500 cc. of water to a milky fluid with a wire beater, 800 grams of ice added, and then a solution of the sodium hydroxide in 500 cc. of water. In this way solution took place almost immediately and a low yield of tetrachloroanthranilic acid due to the hydrolysis of some of the tetrachlorophthalamic acid was prevented. To this mixture the cold sodium hypochlorite solution prepared as described above is added. Sodium hypochlorite is used in ten per cent. excess over the one gram molecule required by the theory for one gram molecule of tetrachlorophthalamic acid. The solution is kept cold by ice added directly and is stirred mechanically. After stirring vigorously for half an hour, the excess of hypochlorite (shown to be present by the blue color produced when a test portion is added to a dilute aqueous solution of aniline) is destroyed by the addition of sufficient sodium bisulphite solution. The solution is then heated for three hours at 70°–80° and decomposed while still hot with an excess of hydrochloric acid. The precipitated acid is quite bulky and is best filtered with suction on a Nutsch filter. The crude acid is then washed with water until free from chlorides. The yield is about ninety per cent.

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[1] See also Graebe: Ber. d. chem. Ges., **35**, 2753.

The pure acid is obtained from the crude product by two methods, one of which was used by Villiger and Blangey. The simpler method is to convert the tetrachloroanthranilic acid into a sodium salt by dissolving it in a boiling ten per cent. solution of sodium carbonate and precipitating the sodium salt by the addition of an equal volume of a saturated solution of sodium chloride. The free acid is obtained by dissolving the sodium salt in hot water and precipitating with a mineral acid. Crystallization of this product from eighty per cent. methyl alcohol gave the pure acid. It has a light yellow color and crystallizes in small needles. About eighty per cent. of the crude material is obtained in this way in the form of the pure acid. The purity of this product was then shown by analyses, after drying to constant weight at 110° in a current of dry air.

Substance Gram	Tenth normal silver nitrate cc.	Chlorine Per cent.
0.1364	19.81	51.50
0.1572	22.87	51.59
	Calculated for $C_7H_3O_2NCl_4$,	51.60

Throughout this investigation chlorine was determined by a modification of the lime method combined with titration according to Volhard.[1] In all cases, unless otherwise stated, the substances prepared for analysis by drying to constant weight were the air-dried products, and the loss was so small as to be negligible.

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[1] Delbridge: This Journal, **41**, 397 (1909).

The second method for the purification of the crude acid depends upon the formation of the formalide discovered by Villiger and Blangey. This formalide, made and purified as described below, was then converted into the sodium salt of tetrachloroanthranilic acid by boiling with an excess of ten per cent. sodium carbonate solution and adding an equal volume of a saturated salt solution. The sodium salt is filtered off and washed on the filter with a saturated salt solution until free from formaldehyde. The pure acid is then obtained from this sodium salt in the same way as in the first method. The yield by this method is only a little less than in the first, since the precipitation of the formalide is nearly quantitative. The acid is best crystallized by dissolving 100 grams in 300 cc. of boiling methyl alcohol, adding 75 cc. of hot water, and allowing to stand. The material obtained by the second method of purification was analyzed after drying to constant weight at 110°.

Substance Gram	Tenth normal silver nitrate cc.	Chlorine Per cent.
0.1478	21.46	51.49
0.1384	20.13	51.58
	Calculated for $C_7H_3O_2NCl_4$,	51.60

The drying apparatus used during this investigation deserves a brief description because of its simplicity and great convenience, although no claim is made for originating the idea.[1]

A Jena-glass tube, 50 cm. in length and 14 mm. in internal diameter, is wrapped with a layer of heavy asbestos paper for 36 cm. of its length so as to leave both ends uncovered for about 7 cm. Ten or twelve feet of manganin wire about 0.5 mm. in diameter is wound along the tube over the protecting layer of asbestos. A piece of air-cell asbestos steam-pipe covering encloses the wiring, the ends of the covering being sealed with asbestos packing. The apparatus is connected with the alternating current 110-volt lighting circuit, the current passing being varied by means of a lamp rheostat. A current of one ampere will maintain a temperature in the tube of about 100°. Temperatures up to 400° are very easily obtained. The substance for examination is put in a small boat and this boat is introduced into the tube. A slow stream of the desired gas is passed through the tube, and the temperature is observed by means of a thermometer laid in the tube and supported at the posterior opening of the tube by a loosely fitting stopper. This apparatus has all the advantages of that described by Delbridge,[1] and in addition eliminates the danger of fire and the inconvenience of water connections, and offers a much more rapid variation of temperature.

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[1] Chamot and Pratt: J. Am. Chem. Soc., **32**, 635 (1910).

Tetrachloroanthranilic acid may be titrated as a monobasic acid, since the amino group has practically no basic properties, and the purity of the substance may be checked by a determination of the molecular weight. For this purpose the sample, after drying to constant weight at 110°, is dissolved in 10 cc. of neutral alcohol, about 0.5 cc. less than the required amount of tenth normal sodium hydroxide added, the solution diluted with water to about 200 cc., and boiled to expel carbon dioxide. After cooling to about 50°, phenoltetrachlorophthalein is added as the indicator, and the titration completed. Tetrachloroanthranilic acid purified by the first method and analyzed as above for chlorine gave the following results:

Substance Gram	Tenth normal sodium hydroxide cc.	Molecular weight
0.6193	22.48	275.5
0.5465	19.85	275.3
	Calculated for $C_7H_3O_2NCl_4$,	274.9

Dimethylaminoazotetrachlorobenzene-o-*carboxylic Acid*

Tetrachloroanthranilic acid is an inner ammonium salt, and hence may be diazotized directly. The diazonium salt thus obtained may be combined with dimethylaniline to form the azo compound.

Materials were used in the following proportions:

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[1] This Journal, **41**, 403 (1909).

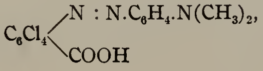
		Grams
Tetrachloroanthranilic acid	0.05 mol.	13.8
Sodium carbonate	0.025 mol.	2.7
Sodium nitrite	0.05 mol. + 0.1 g.	3.6
Hydrochloric acid	0.20 mol.	7.3
Dimethylaniline	0.05 mol.	6.0

The tetrachloroanthranilic acid was dissolved in 200 cc. of a hot soda solution containing 2.7 grams of sodium carbonate. This solution was cooled to 0°, 3.6 grams of solid sodium nitrite added, and then about 20 cc. of approximately six normal hydrochloric acid containing 3.7 grams of hydrochloric acid. The mixture became pasty, so it was stirred up in about 1.5 liters of water cooled with ice. A solution of dimethylaniline hydrochloride, prepared by dissolving 6.0 grams of dimethylaniline in about 20 cc. of six normal hydrochloric acid, was run into the mixture of the diazonium salt, which was stirred mechanically. Potassium hydroxide solution was added to alkaline reaction, the mixture stirred for six hours and allowed to stand overnight. The azo compound was precipitated by the addition of hydrochloric acid, the mixture being heated almost to boiling for one hour to completely decompose the potassium salt. The precipitate was filtered off with suction and washed free from chlorides. The yield was about ninety per cent.

The crude product was purified by dissolving in hot dilute potassium hydroxide, from which solution the potassium salt crystallizes on cooling. This salt was filtered off, dissolved in hot water, and decomposed with hydrochloric acid. The decomposition was rendered complete by boiling for one hour. The precipitated azo compound was filtered off with suction and washed free from chlorides.

After drying to constant weight at 120° the substance was analyzed for chlorine:

Substance Gram	Tenth normal silver nitrate cc.	Chlorine Per cent.
0.1966	19.19	34.61
0.2130	20.82	34.66

Calculated for 

$$C_6Cl_4\left\langle\begin{matrix}N : N.C_6H_4.N(CH_3)_2,\\ COOH\end{matrix}\right.$$

34.85

Dimethylaminoazotetrachlorobenzene-*o*-carboxylic acid is a brilliant red substance, almost insoluble in all ordinary solvents. It is the tetrachloro derivative of methyl red, which was found to possess valuable properties as an indicator.[1] An attempt to use this product as an indicator with tenth normal solutions of ammonium hydroxide, sodium hydroxide and hydrochloric acid showed that the substance was of no value in this respect since the end point was indefinite and not rapidly obtained, the color change was not marked and the reagent lacked sensitiveness to small excesses of the acid or alkali.

Tetrachloroanthranilic Acid Formalide

Villiger and Blangey[2] obtained tetrachloroanthranilic acid formalide by the condensation of tetrachloroanthranilic acid with formaldehyde, and have briefly described the method of preparation and properties of the substance.

During this investigation it was necessary to prepare large quantities of the formalide, the following procedure being found to give the best results: 100 grams of the acid is dissolved in 500 cc. of hot alcohol, 33 grams of thirty-six per cent. formalin added, and the mixture allowed to stand at about 10° for several hours. The formalide crystallizes out in light yellow shimmering leaflets, melting at 213°. Repeated crystallization from alcohol and benzene did not change the color or melting point of the substance, although Villiger and Blangey describe it as being white and melting at 216°. The product which crystallizes out of the reaction mixture is perfectly pure, and a yield of about ninety-five per cent. is obtained. A small quantity of a less pure product may be recovered by concentrating the mother liquor. The corrected melting point of the formalide was found to be 216°. The substance was analyzed for chlorine after drying to constant weight at 110° in hydrogen:

Substance Gram	Tenth normal silver nitrate cc.	Chlorine Per cent.
0.1394	19.42	49.40
	Calculated for $C_8H_3O_2NCl_4$,	49.44

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[1] Rupp and Loose: Ber. d. chem. Ges., **41**, 3905 (1908).

[2] *Ibid.*, **42**, 3551 (1909).

Melting point determinations throughout this investigation were made with an electrically heated Thiele apparatus. Platinum wire was wrapped about the side-arm of the Thiele tube, which was covered with a layer of asbestos to prevent too severe local heating. The wiring was enclosed in a jacket of asbestos fiber cement. The apparatus was connected to the alternating current lighting circuit, the current passing being controlled by a lamp rheostat. The rate of change of temperatures may be easily regulated, and the conditions in different runs maintained uniform without any difficulty. No claim for originality is made in devising this apparatus, which was introduced in this laboratory by Dr. D. S. Pratt.

Tetrachloroanthranilic Acid Formalide Acetate

The imino hydrogen atom of tetrachloroanthranilic acid formalide may be replaced by the acetyl group by heating with acetic anhydride. The acetylation was brought about by boiling 10 grams of the formalide with 150 grams of acetic anhydride for about three hours. On pouring the resultant solution into ice water an oil separated which quickly solidified. The crude product was obtained as a light yellowish brown substance. The yield was ninety per cent.

The crude material was crystallized from alcohol and then from benzene. The melting point of the product from alcohol was not changed by recrystallization from benzene. The acetate crystallizes in colorless rectangular plates melting at 166°.5 (cor.).

The substance crystallized from benzene was dried to constant weight at 110° and analyzed for chlorine:

Substance Gram	Tenth normal silver nitrate cc.	Chlorine Per cent.
0.1691	20.52	43.03
Calculated for $C_8H_2O_2NCl_4(C_2H_3O)$,		43.13

ω-Cyanomethyltetrachloroanthranilic Acid

This cyano compound is referred to very briefly by Villiger and Blangey, who state[1] simply that a solution of potassium cyanide gradually dissolves the formalide with the forma-

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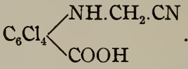
[1] Ber. d. chem. Ges., **42**, 3552 (1909).

tion of the potassium salt of ω-cyanomethyltetrachloroanthranilic acid,  $C_6Cl_4\left\langle\begin{matrix}NH.CH_2.CN\\COOH\end{matrix}\right.$.
They describe the acid as crystallizing in needles melting at 178°, and they state that on boiling with sodium hydroxide it is converted into the corresponding dicarboxylic acid.

The reaction between the formalide and potassiun cyanide must be brought about at comparatively low temperatures since on warming the solution the formalide is decomposed into its components. The best results were obtained by suspending 100 grams of the formalide in one liter of a ten per cent. solution of potassium cyanide. The mixture was stirred mechanically at room temperature for one-half hour, at the end of which time solution was practically complete. The potassium salt of the cyanomethyl compound may crystallize out, but can be easily redissolved by adding more water. The filtered solution was acidified with hydrochloric acid and allowed to stand for several hours. The cyano compound was precipitated in part in crystalline form and in part as an oil which soon solidified. The product was filtered off with suction and washed free from chlorides. The yield was about ninety-five per cent. The reaction is apparently quantitative, but the solubility of the compound in water lowers the yield.

The pure substance was obtained by one crystallization of the crude product from water. Two hundred parts of hot water dissolves one part of the cyano compound, and on cooling most of the material crystallizes out. This product melts at 176° (uncor.). It is almost white with a slight tinge of yellow. It is very readily soluble in cold alcohol, benzene and acetone, less readily soluble in ether and chloroform, insoluble in petroleum ether. The air-dried product was heated to constant weight at 110° in a current of dry air, the loss in weight being inconsiderable, and was then analyzed for chlorine.

Substance Gram	Tenth normal silver nitrate cc.	Chlorine Per cent.
0.1669	21.26	45.17
0.1797	22.89	45.17
	Calculated for $C_9H_4O_2N_2Cl_4$,	45.19

Tetrachlorophenylglycine-o-*carboxylic Acid*

Reference has been made above to the fact that Villiger and Blangey state that ω-cyanomethyltetrachloroanthranilic acid yields the corresponding dicarboxylic acid on hydrolysis. The Badische Anilin- und Soda-Fabrik have patented[1] this method of making tetrachlorophenylglycine-*o*-carboxylic acid. In the patent the substance is described as crystallizing from hot water in white needles melting at 198° with decomposition.

Mauthner and Suida[2] prepared phenylglycine-*o*-carboxylic acid by the reaction between anthranilic acid and monochloroacetic acid in the presence of an excess of sodium carbonate. Later Heumann[3] made it by boiling an aqueous solution of anthranilic acid with monochloroacetic acid without the use of sodium carbonate.

An attempt to prepare tetrachlorophenylglycine-*o*-carboxylic acid by Mauthner and Suida's method showed that the reaction proceeded to some extent at least, but the yield was small and the difficulty of purifying the product rendered the method of no value. The comparative insolubility of tetrachloroanthranilic acid in water prohibited the use of Heumann's method.

The preparation of pure tetrachlorophenylglycine-*o*-carboxylic acid necessitates the complete hydrolysis of pure ω-cyanomethyltetrachloroanthranilic acid. This is best brought about by dissolving the cyano compound in a five per cent. sodium hydroxide solution containing about three molecular parts of sodium hydroxide to one of the cyano compound. The alkaline solution is then heated to boiling and distilled in steam until ammonia no longer distils over. Five hours or more may be required to drive out all the ammonia. An equal volume of water is added, and the mixture filtered to get rid of a small quantity of a greenish blue substance, and also silica from the glass apparatus. The filtrate is acidified with hydrochloric acid and allowed to stand several hours. The precipitate is filtered off and washed free from chlorides. The yield is practically quantitative.

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[1] Chem. Zentralb., **1910**, I, 1564. D. R. P. Kl. 12 q. Nr. 220839.

[2] Monats. Chem., **9**, 728 (1888).

[3] Ber. d. chem. Ges., **23**, 3432 (1890).

The crude product is purified by crystallization from hot water. Boiling water dissolves the acid fairly readily, and on cooling the material is precipitated in the form of very small crystalline needles. The air-dried product is almost white, with a yellow tinge, and melts at 198° (cor.).

The substance crystallized from water and air-dried contains a molecule of water of crystallization, which is given off very readily at 110°. For analysis the material was dried to constant weight at 110° in the drying tube.

Substance Gram	Loss in weight Gram	Loss in weight Per cent.
0.4204	0.0216	5.14
0.4480	0.0229	5.11
	Calculated for $C_9H_5O_4NCl_4.H_2O$,	5.14

Chlorine in the product dried to constant weight at 110° was determined with the following results:

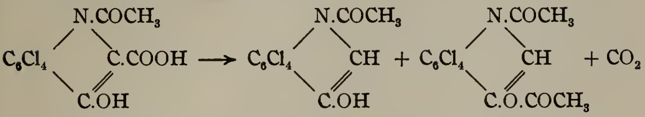
Substance Gram	Tenth normal silver nitrate cc.	Chlorine Per cent.
0.1360	16.42	42.81
0.1939	23.42	42.83
	Calculated for $C_9H_5O_4NCl_4$,	42.61

The analyses apparently show that the material is contaminated with a small quantity of the cyano compound, and this conclusion is supported by a determination of the molecular weight. The air-dried substance was used for this purpose:

Substance Gram	Tenth normal sodium hydroxide cc.	Molecular weight
0.2990	16.83	355.3
0.3610	20.26	356.4
	Calculated for $C_9H_5O_4NCl_4.H_2O$,	350.9

Acetyl Derivative of Tetrachloroindoxyl

The action of acetic anhydride alone on tetrachlorophenylglycine-*o*-carboxylic acid is to eliminate water with the formation of an acetyl derivative of tetrachloroindoxylic acid as described below. If fused sodium acetate be used with the acetic anhydride, the reaction proceeds further, carbon dioxide is removed from the carboxyl group, and mono- and diacetates of tetrachloroindoxyl are formed. This may be represented graphically as follows:



The acetyl group in the monoacetate of tetrachloroindoxyl is represented as being attached to the nitrogen since that is its apparent position in tetrachloroindoxylic acid monoacetate.

For the preparation of these acetates tetrachlorophenylglycine-*o*-carboxylic acid is boiled about two hours with an equal weight of fused sodium acetate and five times its weight of acetic anhydride. The resultant solution is poured into ice water and the mixture stirred mechanically. A brown oil is thrown out which quickly solidifies. This product is then filtered off, washed thoroughly with water, and air-dried. The yield is about seventy-five per cent., calculated on the basis of the diacetate.

The two acetates were obtained from the crude material by fractional crystallization from anhydrous ether. The diacetate is not very soluble in ether and separates out of the hot solution on cooling in well crystallized rectangular plates and prisms, the first crystallization yielding a brown product. In this way about fifteen per cent. of the crude product is obtained as the diacetate. By recrystallizing from ether after boiling the solution with boneblack, the substance was obtained with only a very light blue color and melting at 167° (uncor.). This material, after drying to constant weight at 100°, was analyzed for chlorine:

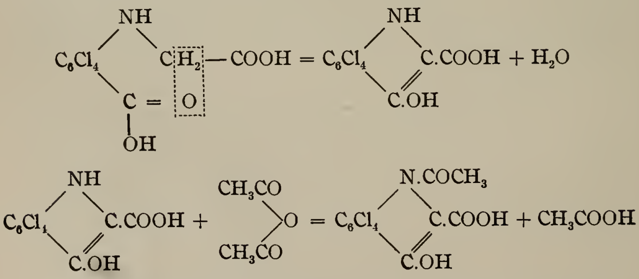
Substance Gram	Tenth normal silver nitrate cc.	Chlorine Per cent.
0.1970	22.06	39.71
Calculated for $C_8HONCl_4(C_2H_3O)_2$,		39.97

The monoacetate is much more soluble in ether than the diacetate, and is obtained by concentrating the solution after the diacetate has been crystallized out. From ether solutions which have been boiled with boneblack it crystallizes in small rounded masses of slender microscopic prisms, perfectly white, and melting at 195° (uncor.). The substance was dried to constant weight at 110° and analyzed for chlorine:

Substance Gram	Tenth normal silver nitrate cc.	Chlorine Per cent.
0.1356	17.14	44.82
Calculated for $C_8H_2ONCl_4(C_2H_3O)$,		45.33

Tetrachloroindoxylic Acid Monoacetate

It seemed probable that acetic anhydride would withdraw a molecule of water from tetrachlorophenylglycine-*o*-carboxylic acid with the formation of tetrachloroindoxylic acid. This reaction apparently takes place, but an acetylated derivative is produced by the continued action of acetic anhydride. This may be represented graphically as follows:



Vorländer and Drescher state[1] that in the case of indoxylic acid monoacetate the acetyl group is attached to the nitrogen atom since the acetylation may be brought about in acid or alkaline solution with the formation of the same substance. Inasmuch as the acetate may be made in alkaline solution it is reasonable to suppose that the acetyl group must be attached to nitrogen. The analogous tetrachloroindoxylic acid monoacetate is therefore represented with a similar structure. Tetrachloroindoxylic acid monoacetate is prepared by boiling

[1] Ber. d. chem. Ges., **34**, 1854 (1901).

tetrachlorophenylglycine-*o*-carboxylic acid with about five times its weight of acetic anhydride for at least one hour, and pouring the resultant solution into ice water. A green oil is thrown out which solidifies in a short time. The mixture is kept stirred mechanically so as to assist in washing out acetic anhydride. The precipitate is filtered off, washed by stirring with water for an hour, and again filtered off. The crude product thus obtained is light green. The yield is variable, but under favorable conditions is about eighty-five per cent. The filtrates, which are strongly acid with acetic acid, hold some of the material in solution, and this may be recovered by evaporating to dryness. The yield is then almost quantitative, but a blue coloring matter is always formed as a by-product.

The crude product is extracted first with a small quantity of benzene to remove most of the coloring matter. Some of the acetate is dissolved by the benzene, but this may be recovered in part by crystallization from the solution. The residue after extraction is crystallized from anhydrous ether. Solvents containing the hydroxyl group, or those not perfectly anhydrous, apparently decompose the acetate to some extent, and highly colored products result. Repeated crystallization from ether yields the pure substance in the form of a crystalline powder, faintly yellowish green, melting at 225° (cor.) with the evolution of gas. The melting point must be determined rapidly because of the decomposition which takes place with consequent lowering of the melting point.

The pure acetate thus obtained was dried to constant weight at 110° and analyzed for chlorine and nitrogen:

Substance Gram	Tenth normal silver nitrate cc.	Chlorine Per cent.
0.1754	19.61	39.65
0.1838	20.62	39.78
Calculated for $C_9H_2O_3NCl_4(C_2H_3O)$,		39.74

Nitrogen was determined by the Kjeldahl method with the following result:

Substance Gram	Tenth normal hydrochloric acid cc.	Nitrogen Per cent.
0.4854	13.45	3.88
Calculated for $C_9H_2O_3NCl_4(C_2H_3O)$,		3.93

The presence of the carboxyl group is indicated by the ease with which the acetate dissolves in cold caustic alkali. The substance does not undergo any change, for on acidification of the alkaline solution the original material is precipitated. Warming with sodium carbonate solution dissolves and saponifies the material, and then with continued heating and shaking in the air a quantitative precipitation of octochloroindigo results.

Silver Salt of Tetrachloroindoxylic Acid Monoacetate

The formation of a stable silver salt of tetrachloroindoxylic acid monoacetate confirms the conclusion that the acetate contains a carboxyl group. The correct conditions for the preparation of this salt were found to be of very great importance if a pure product was to be obtained, since the impure material cannot be purified. The following procedure gave satisfactory results.

One gram of the pure acetate was dissolved in sixty cc. of hot alcohol (distilled over silver nitrate), the solution filtered and allowed to stand for ten hours. At the end of this time the small amount of material that had separated out was filtered off, and to the filtrate was added sixty-five cc. of an alcoholic solution of silver nitrate containing about thirty grams of silver nitrate per liter. This is about four times the amount of silver nitrate required by the theory. A large excess of silver nitrate is, however, essential in order to obtain the pure silver salt. After several days the silver salt, which had slowly crystallized out in ball-like clusters of small needles, was filtered off, washed with cold alcohol, and allowed to air-dry. The product was light grayish green, and analysis for silver showed it to be pure. The air-dried substance contains a molecule of water of crystallization. This was determined by heating the material to constant weight at 110° in carbon dioxide. The condensation of moisture on the walls of the cool part of the tube was observed.

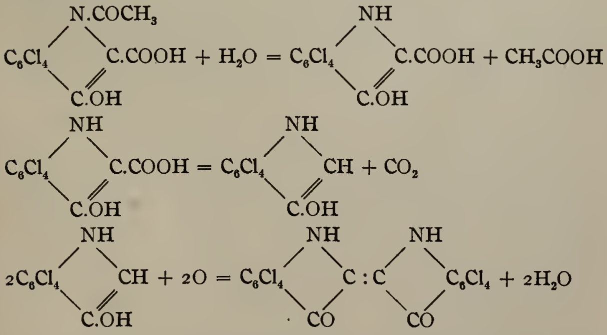
Substance Gram	Loss in weight Gram	Loss in weight Per cent.
0.3755	0.0130	3.46
Calculated for $C_9HO_3NCl_4(C_2H_3O)Ag.H_2O$,		3.74

The portion used for determining the loss of weight was then analyzed for silver. This was carried out by suspending the substance in 100 cc. of boiling alcohol and decomposing with about 10 cc. of dilute nitric acid. The liberated organic acid and the silver nitrate formed are both soluble in alcohol, so that a clear solution was obtained which was light green. The silver nitrate present was titrated directly with tenth normal ammonium sulphocyanate, using ammonium ferric sulphate as indicator. The color of the original solution does not interfere with the sharpness of the end point.

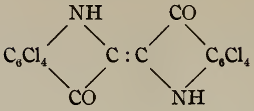
Substance Gram	Tenth normal ammonium sulphocyanate cc.	Silver Per cent.
0.3624	7.74	23.04
Calculated for $C_9HO_3NCl_4(C_2H_3O)Ag$,		23.26

Octochloroindigo

A quantitative precipitation of octochloroindigo occurs when alkaline solutions of tetrachloroindoxylic acid monoacetate are boiled and aërated. The reaction consists in the hydrolysis of the acetate, the elimination of carbon dioxide from the carboxyl group and the oxidation of the resulting tetrachloroindoxyl. This may be represented by the following scheme:



Attention is called to the possibility of stereoisomeric modifications of indigo. The *cis* form of octochloroindigo is shown above; the *trans* form would be represented as follows:



The possible stereoisomerism of indigo has been previously suggested by Falk and Nelson.[1]

Because of the difficulty of purifying octochloroindigo, it is desirable in its preparation to start with pure materials and to use a method which introduces the least possible amount of foreign material. Ammonium hydroxide proved itself to be the most satisfactory alkaline substance to bring about the reaction. Five grams of the pure acetate was dissolved in 250 cc. of four normal ammonium hydroxide with the aid of heat. On continued heating of the solution a green flocculent precipitate was thrown down. The mixture was diluted with water to about two liters and boiled for one hour, while a fairly rapid current of air was passed through it. At the end of this time the green precipitate had entirely changed in color to blue. In order to be sure that the reaction had been complete, twenty-five cc. more of ammonium hydroxide was added and the boiling continued one hour longer. The blue material was quite bulky, and had formed an apparently permanent suspension which did not settle on standing. It was filtered off with suction and washed on the filter with hot water until the wash water left no residue on evaporating to dryness.

The reaction is quantitative, and so starting with pure acetate and removing the ammonium salts by thorough washing, the product obtained by this method should be pure. Octochloroindigo prepared in this way gave the following results for chlorine and nitrogen after drying to constant weight at 110°:

Substance Gram	Tenth normal silver nitrate cc.	Chlorine Per cent.
0.1353	20.07	52.60
0.1443	21.28	52.29
	Calculated for $C_{16}H_2O_2N_2Cl_8$,	52.76

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[1] J. Am. Chem. Soc., **29**, 1739 (1907). See also Ber. d. chem. Ges., **28**, 539 (1895).

Nitrogen was determined by the Kjeldahl method.

Substance Gram	Tenth normal hydrochloric acid cc.	Nitrogen Per cent.
0.2888	10.82	5.25
0.3374	13.26	5.51
	Calculated for $C_{16}H_2O_2N_2Cl_8$,	5.21

Octochloroindigo as prepared by the above method is amorphous, with a rich purple color, and having also a coppery luster which is especially noticeable when the substance is rubbed. Heated at 360° in a current of air it sublimes with some decomposition. The sublimate is finely crystallized in rhombic plates, which are green in thin layers, changing to red and then blue with increasing thickness. The amorphous material dissolves in cold concentrated sulphuric acid with a green color, and the color deepens when the solution is warmed, no other change being apparent. The purple octochloroindigo is precipitated evidently unchanged when this solution is poured into water. The substance dissolves in aniline with a green color. The hot nitrobenzene solution is blue, but on cooling the color changes to green and most of the material crystallizes out, although the crystals are not well developed. It dissolves readily in dimethylaniline with a blue color, and crystallizes from the hot solution on cooling. The product thus obtained is homogeneous, and the fusiform crystals are microscopic in size and very well formed.

Hydroxylamine Derivatives of Tetrachlorophthalic Anhydride

According to Villiger and Blangey dichlorophthalylhydroxylamine (or better, dichlorophthaloxime) may be very easily converted into dichloroanthranilic acid by boiling with a solution of sodium carbonate.[1] This suggested a convenient method for the preparation of tetrachloroanthranilic acid from the corresponding tetrachlorophthaloxime. The peculiar problems presented by the reactions between tetrachlorophthalic anhydride and hydroxylamine seemed to warrant a more detailed study of the subject.

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[1] Ber. d. chem. Ges., **42**, 3543 (1909).

Methyl Ether of Tetrachlorophthaloxime Hydrate

It was supposed that hydroxylamine would react most advantageously if all of the reacting substances were in solution. Materials were used in the following proportions:

		Grams
Hydroxylamine hydrochloride	0.2 mol. + 25 per cent. excess	17.4
Sodium	0.2 mol. + 25 per cent. excess	5.8
Tetrachlorophthalic anhydride	0.2 mol.	57.2

A methyl alcohol solution of hydroxylamine was made by dissolving the hydroxylamine hydrochloride in about 100 cc. of methyl alcohol and pouring this solution into a solution of sodium methylate prepared by dissolving the metallic sodium in 400 cc. of methyl alcohol. The precipitated sodium chloride was filtered off. To the filtrate was added a solution of the anhydride in 250 cc. of methyl alcohol.

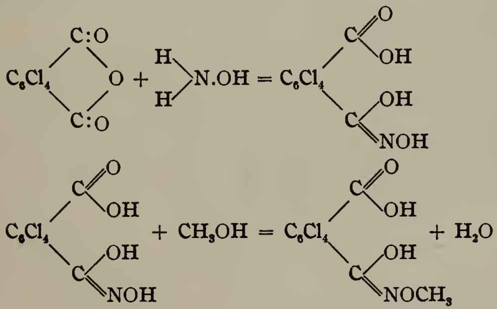
The mixture was boiled for one hour under a return condenser, and then concentrated to about 200 cc. The sodium chloride which was precipitated was filtered off, and the filtrate was diluted strongly with water. This was then evaporated to dryness on the water bath. The residue was extracted with boiling benzene to remove unchanged anhydride. The bulk of the residue was insoluble in benzene. It was fairly readily soluble in methyl alcohol, and crystallized very well from this solvent in small rhombic plates. The crystalline material has a decided yellow color. It melts at 246°–247° (cor.) with decomposition. After drying to constant weight at 110° it was analyzed for chlorine and nitrogen.

Substance Gram	Tenth normal silver nitrate cc.	Chlorine Per cent.
0.1555	18.70	42.64
	Calculated for $C_8H_2O_3Cl_4N(OCH_3)$,	42.61

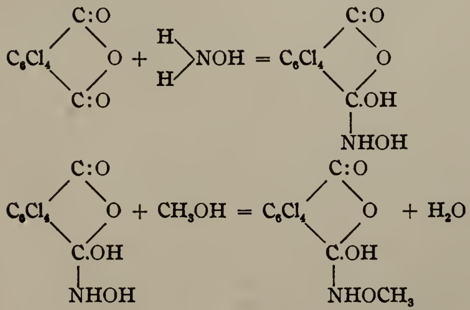
Nitrogen in the hydroxylamine compounds was determined by a modified Kjeldahl method. The portion for analysis was first reduced with nascent hydrogen by boiling for half an hour in the Kjeldahl digestion flask with 3 grams of zinc dust and 50 cc. of thrice normal sulphuric acid. Concentrated sulphuric acid, potassium sulphate and copper sulphate were then added as in the usual method, and the digestion carried on for an hour or so until the reaction was completed.

Substance Gram	Tenth normal hydrochloric acid cc.	Nitrogen Per cent.
0.4743	14.23	4.20
Calculated for $C_8H_2O_3NCl_4(OCH_3)$,		4.21

The methyl ether of tetrachlorophthaloxime hydrate is isomeric with the methyl ester of tetrachlorophthalhydroxamic acid. The formation of either of these substances in the above reaction may be shown by the use of structural formulas as follows:



Methyl Ester of Tetrachloro-phthalhydroxamic Acid



Methyl Ether of Tetrachloro-phthaloxime Hydrate

It seems probable that the latter reaction is the one which actually takes place, since the product does not dissolve in cold caustic alkali, but is converted into an insoluble red substance in aqueous alkaline solutions. Of special importance is the fact that no coloration is produced with ferric chloride. Since hydroxamic acids should always give a violet color with this reagent, it is not likely that this substance is the methyl ester of tetrachlorophthalhydroxamic acid. The material does not lose water when heated to 160°, but at that temperature it sublimes somewhat.

An attempt to prepare a sodium salt resulted in the formation of an impure salt of tetrachlorophthaloxime. Two grams of the ether was dissolved in 200 cc. of methyl alcohol and to the hot solution was added a solution of one gram of fused sodium acetate in 50 cc. of methyl alcohol. The mixture became red, and on concentrating to about 100 cc. and cooling, a red crystalline product was obtained. This was dried in the water oven and then to constant weight at 120° in the drying apparatus. Analysis for chlorine gave the following result:

Substance Gram	Tenth normal silver nitrate cc.	Chlorine Per cent.
0.1644	20.83	44.93
Calculated for $C_8O_3Cl_4NNa$,		43.93
Calculated for $C_8HO_3Cl_4N(OCH_3)Na$,		39.97

It is hardly reasonable to suppose that boiling the sodium salt of the methyl ester of tetrachlorophthalhydroxamic acid with a small quantity of sodium acetate in methyl alcohol solution would result in the elimination of a molecule of methyl alcohol. On the other hand, it seems probable that under similar conditions the methyl ether of tetrachlorophthaloxime hydrate might be hydrolyzed, with the formation of the sodium salt of tetrachlorophthaloxime hydrate, which could then very easily lose water and yield the anhydrous product.

Tetrachlorophthaloxime Hydrate and Tetrachlorophthaloxime

Quite a different product was obtained when water was used as the medium from that which resulted when the reaction between hydroxylamine and tetrachlorophthalic anhydride was carried out in methyl alcohol solution. Recently, in this laboratory, Dr. D. S. Pratt[1] found that in the case of phthalic anhydride the temperature employed exerted a great influence on the nature of the substances formed. If the reaction mixture was heated in the water bath, the phthaloxime obtained was yellow, but if the reaction proceeded at 60° a white isomer was formed. Attempts were made to duplicate these results with tetrachlorophthalic anhydride.

Materials were used in the following proportions:

		Grams
Hydroxylamine hydrochloride	0.2 mol. + 25 per cent. excess	17.4
Sodium carbonate, anhydrous	0.1 mol. + 25 per cent. excess	13.3
Tetrachlorophthalic anhydride	0.2 mol.	57.2

The hydroxylamine hydrochloride was dissolved in 50 cc. of cold water, the sodium carbonate in 50 cc. of hot water. After cooling, the soda solution was poured into the hydroxylamine hydrochloride solution, which was contained in a one liter round-bottomed flask. The anhydride was then rapidly added to this mixture, care being taken at the start, however, not to cause too violent an evolution of gas. The flask was then immersed in an actively boiling water bath and heated in this way without stirring for one hour. The thick, pasty reaction mixture was taken up with water, made decidedly acid with hydrochloric acid and filtered with suction. The residue on the filter was washed with water and then dissolved without drying in methyl alcohol acidified with hydrochloric acid. Acidification is resorted to in order to decompose any sodium salt of the oxime that might have been formed. The reaction product is not very soluble in cold methyl alcohol, and since tetrachlorophthalic anhydride is exceedingly soluble the unchanged anhydride is easily separated from the other material. The yield from the first crystallization was thirty grams, about fifty per cent. of the theoretical. The pure substance was obtained by recrystallizing this product from methyl alcohol.

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[1] This Journal, **47**, 89 (1912).

This material is almost perfectly white, but has a faintly yellow tinge. It crystallizes in small prisms and melts at 254° (cor.). The air-dried material was heated to constant weight at 110°. The formation of water was shown by the condensation of moisture on the cold part of the tube.

Substance Gram	Loss in weight Gram	Loss in weight Per cent.
0.1678	0.0094	5.60
0.4774	0.0271	5.68
	Calculated for $C_8HO_3NCl_4.H_2O$,	5.65

The ease with which this substance loses water was shown by heating it at 50° in a current of hydrogen dried by phosphorus pentoxide. The material came to constant weight in three hours.

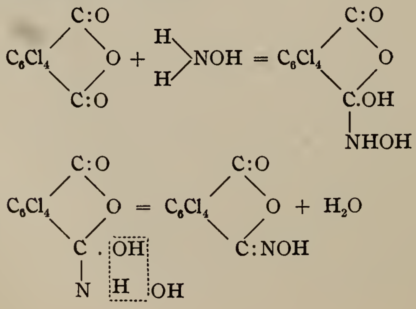
Substance Gram	Loss in weight Gram	Loss in weight Per cent.
0.1703	0.0096	5.64

Standing for twenty-one hours in an evacuated desiccator with phosphorus pentoxide above and below also removed the water, the sample coming to constant weight.

Substance Gram	Loss in weight Gram	Loss in weight Per cent.
0.2649	0.0151	5.70

The anhydrous product was lemon-yellow.

The substance is apparently a stable hydroxylamine addition product of tetrachlorophthalic anhydride. The reaction is represented as follows:



We have called this addition product tetrachlorophthaloxime hydrate. As has been seen, it readily loses a molecule of water and yields the anhydrous tetrachlorophthaloxime. It is analogous to the chloral-hydroxylamine of Hantzsch,[1] which is the hydroxylamine addition product of chloral. The presence of the chlorine in the molecule gives rise to the possibility of the existence of the stable hydrates. Chlorine and nitrogen in the anhydrous substance were determined with the following results:

Substance Gram	Tenth normal silver nitrate cc.	Chlorine Per cent.
0.1576	21.02	47.29
0.1553	20.69	47.24
	Calculated for $C_8HO_3NCl_4$,	47.15

Substance Gram	Tenth normal hydrochloric acid cc.	Nitrogen Per cent.
0.3454	11.84	4.80
0.4494	14.91	4.65
	Calculated for $C_8HO_3NCl_4$,	4.66

Tetrachlorophthaloxime made by heating the crystallized hydrate has the same outward crystal form as the hydrate, but has a pronounced yellow color. It crystallizes from anhydrous benzene with a yellow color. Alkalis convert it as well as the hydrate into the red salts of the oxime, which are insoluble in water. These salts are easily decomposed by warming with caustic alkalis, tetrachlorophthalic acid being formed. Standing with caustic alkalis in the cold, or prolonged boiling with sodium carbonate solution converts the alkali salts into the salts of tetrachlorophthalhydroxamic acid which are colorless and readily soluble in water. No formation of tetrachloroanthranilic acid could be observed. The melting point given for the hydrate is really that of the anhydrous substance since the latter is formed during the heating.

Sodium Salt of Tetrachlorophthaloxime

The yellow oxime was very easily converted into the pure sodium salt. This was accomplished by boiling 5 grams of the oxime in 500 cc. of methyl alcohol with sodium acetate in considerable excess. The sodium salt was precipitated in crystalline form. The mixture was boiled for an hour to insure the complete formation of the salt. The material separated out in rounded clusters of threadlike crystals, dark red in color. This product was filtered off with suction and washed with methyl alcohol.

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[1] Ber. d. chem. Ges., **25**, 702 (1892).

The substance was analyzed for chlorine and sodium after drying to constant weight at 150°.

Substance Gram	Tenth normal silver nitrate cc.	Chlorine Per cent.
0.1528	18.82	43.68
	Calculated for $C_8O_3NCl_4Na$,	43.93

Sodium was determined by fuming down with sulphuric acid. The portion for analysis was contained in a platinum crucible, and to it was added two or three cc. of concentrated sulphuric acid. The crucible was heated in an air bath made of a larger nickel crucible, 85 mm. deep, 105 mm. wide at the top. The platinum crucible was supported on a quartz triangle at a height of about 40 mm. from the bottom of the nickel crucible. The nickel crucible was heated with a moderate sized Bunsen flame, and kept nearly closed by the crucible cover. One cc. of concentrated sulphuric acid was added from time to time as the concentration proceeded until the solution became colorless. An excess of sulphuric acid should always be present to prevent reduction of the sodium sulphate by unburned carbon and consequent loss of sodium by volatilization. The colorless solution was evaporated to dryness in the apparatus, and then the platinum crucible was heated directly for a short time with a Bunsen flame.

Substance Gram	Sodium sulphate Gram	Sodium Per cent.
0.3009	0.0658	7.08
0.2830	0.0640	7.32
	Calculated for $C_8O_3NCl_4Na$,	7.12

Tetrachlorophthaloxime Acetate

The oxime hydrate was boiled for an hour with four or five times its weight of acetic anhydride. The solution was poured into ice water with mechanical stirring, and the product washed with water until practically free from acetic acid. The crude material, which was fairly white, was filtered off and air-dried. When thoroughly dry it was crystallized from anhydrous ether. The pure acetate was obtained by the first crystallization. It crystallizes in white needles, melting at 176° (cor.). The acetate is very easily saponified, even standing with ninety-five per cent. alcohol bringing about the saponification. It may be obtained well crystallized from absolute alcohol, in which it is quite soluble hot, but much less soluble cold. It is excessively soluble in benzene.

The substance from ether was analyzed for chlorine and nitrogen after drying to constant weight in a current of hydrogen.

Substance Gram	Tenth normal silver nitrate cc.	Chlorine Per cent.
0.1762	20.55	41.36
	Calculated for $C_8O_3Cl_4N(C_2H_3O)$,	41.37

The acetate was saponified by gentle warming with potassium hydroxide, and the nitrogen determined in this product in the usual way.

Substance Gram	Tenth normal hydrochloric acid cc.	Nitrogen Per cent.
0.4031	11.81	4.11
	Calculated for $C_8O_3Cl_4N(C_2H_3O)$,	4.09

SUMMARY

The results of this investigation may be briefly stated as follows:

The following substances, which have previously been more or less completely described, have been prepared:

Tetrachloroanthranilic acid
Tetrachloroanthranilic acid formalide
ω-Cyanomethyltetrachloroanthranilic acid
Tetrachlorophenylglycine-*o*-carboxylic acid

The following new substances have been made and studied:

Tetrachloroanthranilic acid formalide acetate
Dimethylaminoazotetrachlorobenzene-*o*-carboxylic acid
Tetrachloroindoxyl monoacetate

Tetrachloroindoxyl diacetate
Tetrachloroindoxylic acid monoacetate
Tetrachloroindoxylic acid monoacetate, silver salt
Octochloroindigo
Methyl ether of tetrachlorophthaloxime hydrate
Tetrachlorophthaloxime hydrate
Tetrachlorophthaloxime (yellow)
Tetrachlorophthaloxime, sodium salt
Tetrachlorophthaloxime acetate

Cornell University
Ithaca, N. Y.
October, 1912

THE CONDUCTIVITY, TEMPERATURE COEFFICIENTS OF CONDUCTIVITY AND DISSOCIATION OF CERTAIN ELECTROLYTES IN AQUEOUS SOLUTION AT 35°, 50° AND 65°

By S. F. Howard and Harry C. Jones

INTRODUCTION

Hosford and Jones[1] and Miss Winston and Jones[2] have measured the conductivity, temperature coefficients of conductivity and dissociation of many electrolytes between 0° and 35°. To extend some of these measurements to higher temperatures, to ascertain whether certain observations made by them at lower temperatures obtain for higher temperatures, and to account, if possible, for certain discrepancies have been the aims of this investigation.

HISTORICAL

Conductivity measurements were made soon after Galvani's discovery of "animal electricity" (1789), and Volta's recognition (1793) of the two classes of conductors, one class conducting apparently without being changed chemically, while conductors of the second class were decomposed by the passage of the current.

Although the study of conductors of the second class did not, for many years, lead to a satisfactory explanation of the phenomena of conduction in solution, certain important relations were discovered.

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[1] This Journal, **46**, 240 (1911).
[2] *Ibid.*, **46**, 368 (1911).

Davy began investigations[1] in 1800 which led to the isolation of the alkali and alkaline earth metals and to the decomposition of water into hydrogen and oxygen. This work and that of others along the same lines led to the electrochemical theories of Davy[2] and Berzelius,[3] and later to the announcement of Faraday's law.[4]

Faraday recognized that solutions of certain substances conducted the current, whereas those of others did not. The former he termed electrolytes and the latter nonelectrolytes. He saw, moreover, that the electrolytes decomposed into charged parts. Those parts which were charged negatively he termed anions, and those that were positively charged were called cations.

A large number of salts, acids and bases were studied by many workers, but the significance of conductivity was not understood until the theory of Arrhenius[5] was proposed in 1887. This theory not only gave added interest and significance to the conductivity of solutions, but brought together under one generalization many of the abnormal measurements of osmotic pressure and of vapor tension and of freezing point lowering. The incentive to make conductivity measurements was greatly increased by the theory, especially as it was pointed out that dissociation could be measured when the conductivity was known at a given dilution and at infinite dilution.

That is, $\alpha = \mu_v/\mu_\infty$, where α is the dissociation, μ_v the conductivity at volume v, and μ_∞ the conductivity at complete dissociation or infinite dilution.

Since the measurements of conductivity can be interpreted in terms of the strengths of acids and bases, and since the reactions between various salts and acids, bases and other salts are conditioned by the amount of ionization, it is evident that a knowledge of these constants is desirable.

[1] Phil. Trans., **1807**, 2.

[2] *Ibid.*, p. 39.

[3] Gilb. Ann., **27**, 270 (1807).

[4] Exp. Researches in Elec., 1833–4.

[5] Z. physik. Chem., **1**, 631 (1887).

The theory of solvation proposed by Jones[1] and confirmed by many lines of experiments conducted by him and his coworkers added further interest to conductivity measurements by explaining very satisfactorily, and for the first time, many apparent abnormalities.

Previous to the work of Kohlrausch,[2] conductivity measurements were made by means of direct currents, but because of polarization the results were not accurate. A considerable number of conductivity measurements have been made since the Kohlrausch method was proposed, but little systematic work was done until Jones and his coworkers took up the problem.

The work in this laboratory has been carried on systematically, measurements being made upon solutions of most of the more common electrolytes, at temperatures from 0° to 65°, and at convenient and uniform dilutions. When the work as a whole is completed there will be obtainable many data which have heretofore not been available.

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[1] 1. Jones and Chambers: This Journal, **23**, 89 (1900). 2. Chambers and Frazer: *Ibid.*, **23**, 512 (1900). 3. Jones and Getman: *Ibid.*, **27**, 433 (1902). 4. Jones and Getman: Z. physik. Chem., **46**, 244 (1903); Phys. Rev., **18**, 146 (1904). 5. Jones and Getman: This Journal, **31**, 303 (1904). 6. Jones and Getman: Z. physik. Chem., **49**, 385 (1904). 7. Jones and Getman: Ber. d. chem. Ges., **37**, 1511 (1904). 8. Jones and Getman: This Journal, **32**, 308 (1904). 9. Jones and Getman: *Ibid.*, **32**, 338 (1904). 10. Jones and Bassett: *Ibid.*, **33**, 534 (1905). 11. Jones: J. chim. phys., **3**, 455 (1905). 12. Jones and Bassett: Z. physik. Chem., **52**, 231 (1905). 13. Jones and Bassett: This Journal, **34**, 291 (1905). 14. Jones: Z. physik. Chem., **35**, 385 (1906). 15. Jones and McMaster: This Journal, **35**, 136 (1906). 16. Jones: *Ibid.*, **35**, 445 (1906). 17. Jones and Uhler: *Ibid.*, **37**, 126 (1907). 18. Jones and Uhler: *Ibid.*, **37**, 244 (1907). 19. Jones and Pearce: *Ibid.*, **38**, 683 (1907). 20. Jones and Stine: *Ibid.* **39**, 313 (1908). 21. Jones and Anderson: P. Am. Phil. Soc., **47**, 276 (1908). 22. Jones and Jacobson: This Journal, **40**, 355 (1908). 23. Jones: *Ibid.*, **41**, 19 (1909). 24. Jones and Anderson: *Ibid.*, **41**, 163 (1909). 25. Jones and Anderson: P. Am. Phil. Soc., **48**, 194 (1909). 26. Jones and Strong: This Journal, **43**, 37 (1910). 27. Jones and Strong: Physik. Z., **10**, 499 (1909). 28. Jones and Strong: This Journal, **43**, 224 (1910). 29. Jones and Strong: Phil. Mag., **1910**, 566. 30. Jones: Z. physik. Chem., **74**, 325 (1911). 31. Jones and Schmidt: This Journal, **42**, 37 (1909). 32. White and Jones: *Ibid.*, **42**, 520 (1909). 33. Clover and Jones: *Ibid.*, **43**, 187 (1910). 34. White and Jones: *Ibid.*, **44**, 159 (1910). 35. West and Jones: *Ibid.*, **44**, 508 (1910). 36. Jones: J. chim. phys., **9**, 217 (1911). 37. Winston: This Journal, **45**, 547 (1911). 38. Wightman and Jones: *Ibid.*, **46**, 56 (1911). 39. Hosford and Jones: *Ibid.*, **46**, 240 (1911). 40. Winston and Jones: *Ibid.*, **46**, 368 (1911). 41. Jones: Carnegie Inst. of Wash., Pub. No. **60** (1907). 42. Jones: *Ibid.*, No. **80** (1907). 43. Jones and Anderson: *Ibid.*, No. **110** (1909). 44. Jones and Strong: *Ibid.*, No. **130** (1910). 45. Jones and Strong: *Ibid.*, No. **160** (1911).

[2] Wied. Ann., **6**, 145 (1879).

EXPERIMENTAL

Preparation of Material.—Kahlbaum's purest salts were used in nearly all cases, and were recrystallized several times from "conductivity water" prepared according to the method of Jones and Mackay.[1]

Apparatus and Method.—The method of Kohlrausch was used, and the apparatus in general has been described by other workers in this laboratory. The bridge was of the Kohlrausch slide wire type, made and standardized by Leeds and Northrup, and graduated in half-millimeters. The cells are described by Clover and Jones[2] and by Jones and West,[3] and the constants were determined every two weeks by means of a 0.02 N solution of potassium chloride, whose conductivity was taken as 129.7. A 0.002 N solution of potassium chloride was used for the cells whose plates were close together, its conductivity having been determined in a cell whose constant had been found by using the 0.02 N solution. Similarly, a 0.0005 N solution of potassium chloride was used to determine the constant for the water cell.

Because of the small conductivity of the water, as compared with that of even the most dilute solutions, a special "water cell" was used which differed from the other cells in having much larger electrodes. These electrodes consisted of two concentric cylinders of platinum from 2.5 to 2.75 inches high, held in position by small pieces of fusible glass, in such a manner that the inner and outer cylinders were a sixteenth of an inch or less apart.

Conductivity measurements were made at 35°, 50° and 65°, at the same dilutions as were used by other workers at the lower temperatures.

Two baths were employed, a smaller one for 35° and 65°, and a larger which was kept at approximately 50° day and night, and carefully adjusted for 50° during the measurements. When the cells were not in use they were kept in the larger bath in order to eliminate such changes in cell constants as would be produced by different temperatures. Each bath was made of galvanized iron, and consisted of two cylindrical vessels which were concentric, with asbestos cement between the vertical walls, and which had a common bottom.

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[1] This Journal, **19**, 91 (1897).

[2] *Ibid.*, **43**, 192 (1910).

[3] *Ibid.*, **44**, 510 (1910).

The inner vessel for the smaller bath was 10 inches deep and 12 inches in diameter, while the outer was 10.5 inches deep and 16 inches in diameter. For the larger bath the inner vessel was 14 inches deep and 14 inches in diameter, the outer 14.5 inches deep and 18 inches in diameter.

"Asbestos wood" covers, $^1/_8$ inch thick, treated with a small amount of paraffin, were used on the baths. They were octagonal in shape, just large enough to extend over the rims of the outer vessel of each bath. Two circular holes, 2.25 inches in diameter, were cut in each cover, one in the center for the stirrer and thermometer, the other nearer the edge and over the line of cells supported in the bath. Brass guides were fastened to the edges so that the covers could be rotated upon the rims of the outer vessels.

The covers were cut and hinged so that the larger part was about two-thirds, and the smaller one-third of the whole. In the smaller part was the hole referred to, through which the wires were passed from the coil, etc., to each cell. The hole in the center was covered with a circular piece of asbestos wood, cut in two and fastened together after making small holes in it for the thermometer and stirrer. This did not revolve with the large cover.

Obviously the cover should be so constructed and fitted that as much heat as possible is retained in the bath with minimum evaporation of the water. On the other hand, it was necessary to remove the cells from time to time to inspect them and to eliminate air bubbles. It was also necessary to insert the wires into the cells and to change them to other cells. Thus, the cover must prevent loss of heat, and at the same time the cells must be accessible, and it is believed that these results were satisfactorily attained.[1]

The gutta percha supports used for lower temperatures were found to soften and warp at higher temperatures, and, therefore, supports made entirely of brass were used. Each holder supports three cells and the changes from one bath to another were made three cells at a time. If a bath was to be left at a certain temperature for a considerable time, a mercury thermoregulator was used, but usually a constant temperature was satisfactorily maintained within 0°.1 to 0°.2 by means of two low-form burners, one very small which could be carefully regulated, and the other to bring the bath rapidly to the correct temperature.

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[1] Mr. E. J. Shaeffer and Howard have been carrying on similar work, using the same cells and apparatus. Jointly they devised and constructed the accessories to the bath here described.

The cells were connected with a switch by means of a pair of pliable copper wires (No. 14) two or three feet long, and the switch in turn was connected with the other apparatus by larger wires.

Except for the modifications noted, the work was carried on similarly to that described by earlier workers.

Preparation of Solutions.—A few solutions were made by weighing out the purified salt and adding the correct amount of solvent. In most cases, however, a solution stronger than the strongest to be measured was made up and analyzed, and dilutions prepared from this.

The measuring apparatus was calibrated at 20°. When the "mother solution" was prepared, sufficient salt or salt solution was taken and placed in a measuring flask, and this was kept in the 50° bath for an hour and then water at the same temperature added to the mark. On cooling to 20° this was measured into the different burettes and flasks, and the desired volumes made up. The readings at 35° were multiplied by the factor 0.994 and those at 65° by the factor 1.0076.

Every one of the following results is the average of at least three measurements. A general discussion follows the tables:

Table I.—Sodium Ferrocyanide, $Na_4Fe(CN)_6.12H_2O$

The original solution was made by direct weighing of the anhydrous salt.

Molecular Conductivity

V	35°	50°	65°
8	306.61	386.89	469.609
16	330.29	418.91	508.689
32	380.43	487.25	593.800
128	457.93	594.44	727.678
512	554.43	730.35	909.856
1024	591.86	781.99	979.348
2048	614.64	804.49	1000.842
4096	633.20	803.01	968.996

Temperature Coefficients

	35°–50°		50°–65°	
V	Cond. units	Per cent.	Cond. units	Per cent.
8	5.35	1.74	5.51	1.42
16	5.89	1.78	5.99	1.43
32	7.12	1.87	7.10	1.46
128	9.10	1.98	8.88	1.49
512	11.73	2.11	11.90	1.63
1024	12.68	2.14	13.16	1.68
2048	12.66	2.06	13.09	1.63
4096	11.33	1.78	11.06	1.38

Percentage Dissociation

V	35°	50°	65°
8	48.42	48.09	46.92
16	52.16	52.07	50.83
32	60.08	60.57	59.33
128	72.32	73.89	72.71
512	87.56	90.78	90.91
1024	93.47	97.20	97.85
2048	97.07	100.00	100.00
4096	100.00	99.82	96.82

Table II.—Potassium Carbonate, K_2CO_3

The original solution was made by direct weighing of the salt after heating for several hours at 110°.

Molecular Conductivity

V	35°	50°	65°
2	158.35	199.34	228.63
8	191.45	237.57	291.17
16	216.87	278.66	341.86
32	228.87	296.51	369.42
128	263.89	340.18	424.50
512	284.36	378.64	468.12
2048	279.17	349.12	423.18
4096	253.01	314.61	376.53

Temperature Coefficients

	35°–50°		50°–65°	
V	Cond. units	Per cent.	Cond. units	Per cent.
2	2.73	1.73	1.95	0.98
8	3.07	1.60	2.57	1.08
16	4.12	1.90	4.21	1.51
32	4.51	1.97	4.86	1.64
128	5.09	1.93	5.62	1.32
512	6.29	2.21	5.89	1.26
2048	4.66	1.66	4.94	1.17
4096	4.11	1.62	4.13	1.10

Percentage Dissociation

V	35°	50°	65°
2	55.69	52.65	48.84
8	67.33	62.74	62.20
16	76.26	73.59	73.03
32	80.48	78.31	78.92
128	92.80	89.84	90.68
512	100.00	100.00	100.00
2048	98.17	92.20	90.40
4096	88.97	83.09	80.43

Table III.—Potassium Permanganate, $KMnO_4$

The permanganate solution was standardized volumetrically against potassium tetroxalate.

Molecular Conductivity

V	35°	50°	65°
8	126.75	159.16	193.58
32	136.68	171.71	208.58
128	144.75	181.98	222.22
512	146.39	185.19	226.46
1024	145.39	182.45	215.95
2048	147.12	183.16	215.22
4096	146.26	178.59	205.22

Temperature Coefficients

	35°–50°		50°–65°	
V	Cond. units	Per cent.	Cond. units	Per cent.
8	2.16	1.70	2.29	1.44
32	2.32	1.70	2.46	1.43
128	2.48	1.71	2.68	1.47
512	2.59	1.77	2.75	1.48
1024	2.47	1.70	2.23	1.22
2048	2.40	1.63	2.14	1.17
4096	2.16	1.48	1.78	0.997

Percentage Dissociation

V	35°	50°	65°
8	86.15	85.94	85.48
32	92.90	92.72	92.10
128	98.39	98.27	98.13
512	99.50	100.00	100.00
1024	98.82	98.52	95.36
2048	100.00	98.90	95.04
4096	99.42	96.44	90.62

Table IV.—Dipotassium Phosphate, K_2HPO_4

The original solution was standardized by determining the phosphoric acid as magnesium pyrophosphate.

Molecular Conductivity

V	35°	50°	65°
2	139.86	175.07	212.29
8	184.28	234.37	285.21
32	221.75	285.70	350.72
128	252.43	321.93	396.74
512	290.51	346.06	427.15
1024	275.92	347.79	434.00
2048	268.44	344.92	432.97
4096	265.74	340.29	426.20

Temperature Coefficients

	35°–50°		50°–65°	
V	Cond. units	Per cent.	Cond. units	Per cent.
2	2.35	1.68	2.48	1.42
8	3.34	1.81	3.39	1.44
32	4.26	1.92	4.33	1.52
128	4.63	1.83	4.32	1.34
512	3.70	1.27	5.41	1.56
1024	4.78	1.73	5.75	1.65
2048	5.09	1.90	5.87	1.70
4096	4.97	1.87	5.73	1.68

Percentage Dissociation

V	35°	50°	65°
2	48.14	50.34	48.91
8	63.43	67.39	65.72
32	76.33	82.15	80.81
128	86.89	92.56	91.42
512	100.00	99.50	98.42
1024	94.98	100.00	100.00
2048	92.40	99.17	99.77
4096	91.48	97.84	98.20

Table V.—Dipotassium Phosphate, K_2HPO_4

These readings were made *one month later* from solutions made up from the same mother solution as those of Table IV.

Molecular Conductivity

V	35°	50°	65°
2	197.54	247.08	298.51
8	315.66	401.01	487.30
32	334.60	427.58	519.59
128	372.53	478.50	590.59
512	414.08	533.40	659.24
1024	426.42	545.14	676.53
2048	422.17	545.44	671.96
4096			

Temperature Coefficients

	35°–50°		50°–65°	
V	Cond. units	Per cent.	Cond. units	Per cent.
2	3.30	1.66	3.43	1.39
8	5.66	1.79	5.75	1.43
32	6.20	1.85	6.14	1.44
128	7.07	1.90	7.45	1.56
512	7.95	1.92	8.39	1.57
1024	7.91	1.85	8.76	1.61
2048	8.22	1.95	8.43	1.55

Percentage Dissociation

V	35°	50°	65°
2	46.33	45.30	44.12
8	74.02	73.52	72.03
32	78.47	78.39	76.80
128	87.36	87.73	87.30
512	97.11	97.79	97.44
1024	100.00	99.95	100.00
2048	99.00	100.00	99.32

Table VI.—Potassium Sodium Sulphate, $KNaSO_4$

The solution was made by weighing the dry salt.

Molecular Conductivity

V	35°	50°	65°
4	182.65	225.23	272.73
8	199.55	251.17	305.40
32	237.05	301.65	367.39
128	270.35	345.97	424.23
512	291.20	375.47	455.59
1024	297.42	382.60	469.31
2048	307.87	395.50	489.05
4096	330.07	427.44	521.52

Temperature Coefficients

	35°–50°		50°–65°	
V	Cond. units	Per cent.	Cond. units	Per cent.
4	2.84	1.55	3.17	1.41
8	3.44	1.72	3.61	1.44
32	4.31	1.82	4.38	1.45
128	5.04	1.86	5.22	1.51
512	5.62	1.93	5.34	1.42
1024	5.68	1.91	5.78	1.51
2048	5.84	1.90	6.24	1.58
4096	6.09	1.85	6.35	1.46

Percentage Dissociation

V	35°	50°	65°
4	55.34	52.69	52.30
8	60.46	58.76	58.56
32	71.82	70.57	70.45
128	81.91	80.94	81.34
512	88.22	87.84	87.36
1024	90.11	89.51	89.99
2048	93.17	92.53	93.77
4096	100.00	100.00	100.00

Table VII.—Potassium Chromium Sulphate (Violet), $KCr(SO_4)_2.12H_2O$

The original solution was standardized by determining the sulphuric acid as barium sulphate.

Molecular Conductivity

V	35°	50°	65°
8	166.97	201.86	242.04
16	183.28	219.21	276.73
32	225.77	271.70	339.90
128	288.11	363.28	467.30
512	404.13	499.67	658.91
1024	465.44	586.07	785.37
2048	546.86	701.81	928.44
4096	637.39	818.02	1082.97

Temperature Coefficients

	35°–50°		50°–65°	
V	Cond. units.	Per cent.	Cond. units	Per cent.
8	2.33	1.39	2.68	1.33
16	2.39	1.30	3.83	1.28
32	3.06	1.36	4.55	1.67
128	4.34	1.46	6.93	1.91
512	6.37	1.57	10.62	2.15
1024	8.04	1.73	13.29	2.27
2048	10.33	1.89	15.11	2.15
4096	12.04	1.89	17.66	2.16

Percentage Dissociation

V	35°	50°	65°
8	26.20	24.68	22.35
16	28.75	26.80	25.55
32	35.42	33.21	31.39
128	46.77	44.41	43.15
512	63.40	61.08	60.84
1024	73.02	71.65	72.52
2048	85.80	85.79	85.73
4096	100.00	100.00	100.00

Table VIII.—Potassium Chromium Sulphate (Green)

This solution was made by heating the original violet solution at 80° for at least eight hours.

Molecular Conductivity

V	35°	50°	65°
8	193.98	221.47	248.10
16	219.16	252.44	279.35
32	270.38	318.16	352.59
128	357.98	437.81	485.99
512	474.89	618.30	699.33
1024	487.61	658.54	771.94
2048	535.90	753.80	903.28
4096	584.29	848.62	1017.05

Temperature Coefficients

	35°–50°		50°–65°	
V	Cond. units	Per cent.	Cond. units	Per cent.
8	1.83	0.94	1.78	0.80
16	2.22	1.01	1.79	0.71
32	3.19	1.18	2.30	0.72
128	5.32	1.49	3.21	0.73
512	9.56	2.01	5.40	0.87
1024	11.39	2.34	7.56	1.15
2048	14.53	2.71	9.97	1.37
4096	17.62	3.02	11.23	1.32

Percentage Dissociation

V	35°	50°	65°
8	33.20	26.10	24.39
16	37.51	29.75	27.47
32	46.27	37.49	34.67
128	61.27	51.59	47.78
512	81.28	72.86	68.76
1024	83.45	77.60	75.90
2048	91.72	88.83	88.81
4096	100.00	100.00	100.00

Table IX.—Potassium Nickel Sulphate, $K_2Ni(SO_4)_2.6H_2O$

The sulphuric acid was determined as barium sulphate.

Molecular Conductivity

V	35°	50°	65°
8	273.53	343.45	407.67
32	349.04	438.23	527.29
128	432.10	547.33	659.73
512	513.77	655.16	798.45
1024	545.16	695.98	850.21
2048	587.40	752.22	927.00
4096	607.93	785.94	960.54

Temperature Coefficients

	35°–50°		50°–65°	
V	Cond. units	Per cent.	Cond. units	Per cent.
8	4.66	1.70	4.28	1.25
32	5.95	1.70	5.94	1.36
128	7.68	1.78	7.49	1.37
512	9.43	1.84	9.55	1.46
1024	10.05	1.84	10.28	1.48
2048	10.99	1.87	11.65	1.55
4096	11.87	1.95	11.64	1.48

Percentage Dissociation

V	35°	50°	65°
8	44.99	43.70	42.44
32	57.42	55.76	54.90
128	71.08	68.64	68.68
512	84.51	83.36	83.13
1024	89.68	88.55	88.51
2048	96.62	95.71	96.51
4096	100.00	100.00	100.00

Table X.—Ammonium Chromium Sulphate (*Violet*), $NH_4Cr(SO_4)_2.12H_2O$

The sulphuric acid was determined as barium sulphate.

Molecular Conductivity

V	35°	50°	65°
8	169.80	204.92	244.97
16	197.87	239.15	288.79
32	228.59	274.46	333.50
128	302.72	369.58	459.09
512	410.17	508.79	648.99
1024	483.10	604.32	754.79
2048	577.37	713.72	897.35
4096	671.17	853.42	1050.26

Temperature Coefficients

	35°–50°		50°–65°	
V	Cond. units	Per cent.	Cond. units	Per cent.
8	2.34	1.38	2.67	1.30
16	2.75	1.39	3.31	1.38
32	3.06	1.34	3.94	1.44
128	4.46	1.47	5.90	1.60
512	5.91	1.44	9.35	1.84
1024	8.08	1.67	10.03	1.66
2048	9.09	1.57	12.24	1.71
4096	12.15	1.81	13.12	1.54

Percentage Dissociation

V	35°	50°	65°
8	25.30	24.01	23.32
16	29.48	28.02	27.50
32	34.06	32.16	31.75
128	45.10	43.31	43.71
512	61.11	59.63	61.79
1024	71.98	70.81	71.87
2048	86.02	83.63	85.44
4096	100.00	100.00	100.00

Table XI.—Ammonium Chromium Sulphate (Green)

This solution was made by heating the original violet solution at 80° for at least eight hours.

Molecular Conductivity

V	35°	50°	65°
8	193.98	223.33	250.70
16	229.79	268.08	299.59
32	268.04	316.57	352.20
128	355.62	436.52	489.76
512	446.13	585.31	673.80
1024	492.16	658.87	789.57
2048	537.15	757.75	924.29
4096	589.81	868.79	1061.73

Temperature Coefficients

	35°–50°		50°–65°	
V	Cond. units	Per cent.	Cond. units	Per cent.
8	1.96	1.01	1.82	0.81
16	2.55	1.11	2.10	0.78
32	3.24	1.21	2.38	0.75
128	5.39	1.52	3.55	0.81
512	9.28	2.08	5.90	1.01
1024	11.11	2.26	8.71	1.32
2048	14.71	2.74	11.10	1.46
4096	18.60	3.15	12.86	1.48

Percentage Dissociation

V	35°	50°	65°
8	32.89	25.71	23.61
16	38.96	30.86	28.32
32	45.45	36.44	33.17
128	60.29	50.24	46.13
512	75.64	67.37	63.46
1024	83.44	75.84	74.37
2048	91.07	87.22	87.06
4096	100.00	100.00	100.00

Table XII.—Calcium Bromide, $CaBr_2$

The calcium was determined as the oxide by ignition of the oxalate.

Molecular Conductivity

V	35°	50°	65°
2	176.49	219.99	262.05
8	220.47	278.91	339.40
16	233.42	296.41	362.30
32	250.41	318.70	391.68
128	273.47	350.57	431.83
512	288.84	375.49	458.67
1024	300.23	386.64	477.18
2048	303.99	390.98	487.30

Temperature Coefficients

	35°–50°		50°–65°	
V	Cond. units	Per cent.	Cond. units	Per cent.
2	2.90	1.64	2.84	1.30
8	3.90	1.77	4.03	1.44
16	4.20	1.80	4.39	1.48
32	4.55	1.82	4.86	1.52
128	5.14	1.88	5.42	1.55
512	5.77	1.99	5.54	1.48
1024	5.76	1.92	6.03	1.56
2048	5.80	1.91	6.42	1.64

Percentage Dissociation

V	35°	50°	65°
2	58.06	56.27	53.78
8	72.53	71.34	69.65
16	76.79	75.81	74.35
32	82.37	81.51	80.38
128	89.96	89.66	88.62
512	95.02	96.04	94.12
1024	98.76	98.89	97.92
2048	100.00	100.00	100.00

Table XIII.—Calcium Chromate, $CaCrO_4$

The mother solution was standardized by determining the calcium oxide from ignition of the oxalate.

Molecular Conductivity

V	35°	50°	65°
8	128.60	158.03	187.81
16	145.08	180.02	214.73
32	163.29	204.40	243.98
128	207.22	261.25	315.84
512	247.52	315.98	387.01
1024	261.40	332.29	401.22
2048	269.70	344.41	418.31
4096	266.11	340.24	419.18

Temperature Coefficients

	35°–50°		50°–65°	
V	Cond. units.	Per cent.	Cond. units.	Per cent.
8	1.96	1.52	1.99	1.26
16	2.37	1.63	2.27	1.26
32	2.74	1.68	2.64	1.29
128	3.60	1.74	3.64	1.39
512	4.56	1.84	4.74	1.50
1024	4.73	1.81	4.60	1.38
2048	4.98	1.85	4.93	1.43
4096	4.94	1.86	5.26	1.55

Percentage Dissociation

V	35°	50°	65°
8	47.68	45.88	44.80
16	53.79	52.44	51.23
32	60.55	59.35	58.20
128	76.83	75.85	75.35
512	91.78	91.75	92.33
1024	96.92	96.48	95.72
2048	100.00	100.00	99.79
4096	98.67	98.79	100.00

Table XIV.—Zinc Nitrate, $Zn(NO_3)_2$

The zinc was determined as zinc oxide.

Molecular Conductivity

V	35°	50°	65°
4	168.65	211.18	258.65
8	188.01	238.25	289.67
32	218.36	280.00	343.09
128	243.53	312.91	384.97
512	260.98	336.48	415.20
1024	267.95	347.35	428.50
2048	276.37	352.62	434.82
4096	281.02	359.97	445.53

Temperature Coefficients

	35°–50°		50°–65°	
V	Cond. units	Per cent.	Cond. units	Per cent.
4	2.84	1.68	3.16	1.50
8	3.35	1.78	3.43	1.44
32	4.11	1.88	4.21	1.50
128	4.63	1.90	4.80	1.53
512	5.03	1.93	5.22	1.55
1024	5.29	1.97	5.41	1.56
2048	5.08	1.84	5.48	1.55
4096	5.26	1.87	5.70	1.58

Percentage Dissociation

V	35°	50°	65°
4	60.01	58.67	58.05
8	66.90	66.19	65.02
32	77.70	77.78	77.01
128	86.66	86.93	86.41
512	92.87	93.47	93.19
1024	95.35	96.49	96.18
2048	98.35	97.96	97.60
4096	100.00	100.00	100.00

Table XV.—Zinc Acetate, $Zn(C_2H_3O_2)_2 \cdot 3H_2O$

The zinc was determined as zinc oxide.

Molecular Conductivity

V	35°	50°	65°
8	77.18	90.46	100.61
32	122.60	149.28	172.86
128	162.36	205.63	243.46
512	188.21	242.85	298.49
1024	190.99	246.67	298.74
2048	198.90	257.81	319.47
4096	198.27	259.11	320.44

Temperature Coefficients

	35°–50°		50°–65°	
V	Cond. units	Per cent.	Cond. units	Per cent.
8	0.89	1.15	0.68	0.75
32	1.78	1.45	1.57	1.05
128	2.88	1.77	2.52	1.23
512	3.64	1.93	3.71	1.53
1024	3.71	1.94	3.47	1.41
2048	3.93	1.98	4.11	1.59
4096	4.06	2.05	4.09	1.58

Percentage Dissociation

V	35°	50°	65°
8	38.80	34.91	31.40
32	61.63	57.61	53.94
128	81.63	79.36	75.98
512	94.63	93.72	93.15
1024	96.02	95.20	93.23
2048	100.00	99.50	99.70
4096	99.68	100.00	100.00

Table XVI.—Lead Chloride, $PbCl_2$

The salt was dried and weighed directly.

Molecular Conductivity

V	35°	50°	65°
64	223.16	277.13	331.22
128	251.27	314.89	379.39
512	290.75	370.26	452.75
1024	305.58	387.25	476.90
2048	316.59	412.06	502.84
4096	326.33	416.97	515.18

Temperature Coefficients

	35°–50°		50°–65°	
V	Cond. units	Per cent.	Cond. units	Per cent.
64	3.60	1.61	3.61	1.30
128	4.24	1.69	4.30	1.37
512	5.30	1.82	5.50	1.49
1024	5.44	1.78	5.98	1.54
2048	6.36	2.01	6.05	1.47
4096	6.04	1.85	6.57	1.58

Percentage Dissociation

V	35°	50°	65°
64	68.39	66.46	64.29
128	77.01	75.52	73.64
512	89.11	88.80	87.88
1024	93.65	92.87	92.57
2048	97.03	98.82	97.60
4096	100.00	100.00	100.00

Table XVII.—Lead Acetate, $Pb(C_2H_3O_2)_2 \cdot 3H_2O$

The lead was determined as lead sulphate.

Molecular Conductivity

V	35°	50°	65°
4	27.00	34.57	41.42
8	37.98	48.18	58.12
32	66.83	84.36	102.61
128	105.95	132.56	158.54
512	152.89	191.61	228.18
1024	170.98	214.38	255.53
2048	191.50	242.06	289.42
4096	204.87	260.97	315.50

Temperature Coefficients

	35°–50°		50°–65°	
V	Cond. units	Per cent.	Cond. units	Per cent.
4	0.51	1.89	0.46	1.33
8	0.68	1.79	0.66	1.37
32	1.17	1.75	1.22	1.45
128	1.77	1.67	1.73	1.31
512	2.58	1.69	2.44	1.27
1024	2.89	1.69	2.74	1.28
2048	3.37	1.76	3.16	1.36
4096	3.41	1.66	3.64	1.39

Percentage Dissociation

V	35°	50°	65°
4	13.18	13.25	13.13
8	18.54	18.46	18.42
32	32.62	32.33	32.52
128	51.72	50.80	50.25
512	74.63	73.42	72.32
1024	83.46	82.15	80.99
2048	93.47	92.75	91.73
4096	100.00	100.00	100.00

Table XVIII.—Nickel Acetate, $Ni(C_2H_3O_2)_2$

The nickel was determined as nickel oxide.

Molecular Conductivity

V	35°	50°	65°	
2	47.95	60.45	72.22	Hydrolysis
8	91.99	115.65	138.32	
16	114.02	144.47	171.27	
32	134.85	171.78	206.39	
128	172.52	223.26	272.67	
512	196.30	256.95	316.98	
1024	206.88	270.18	336.46	
2048	212.66	276.44	247.66	

Temperature Coefficients

	35°–50°		50°–65°	
V	Cond. units	Per cent.	Cond. units	Per cent.
2	0.32	1.73	0.78	1.29
8	1.58	1.72	1.49	1.29
16	2.03	1.78	1.79	1.24
32	2.56	1.90	2.31	1.34
128	3.38	1.96	3.29	1.47
512	4.04	2.06	4.00	1.56
1024	4.22	2.04	4.42	1.64
2048	4.25	2.00	4.73	1.71

Percentage Dissociation

V	35°	50°	65°
2	22.55	21.87	20.77
8	43.26	41.84	39.79
16	53.62	52.26	49.26
32	63.41	62.14	59.37
128	81.12	80.76	78.43
512	92.31	92.95	91.18
1024	97.18	97.74	96.78
2048	100.00	100.00	100.00

Table XIX.—Uranyl Chloride, $UO_2Cl_2.H_2O$

The uranium in the chloride, nitrate, sulphate and acetate was precipitated with ammonia and weighed as the oxide U_3O_8.

Molecular Conductivity

V	35°	50°	65°
4	160.71	198.60	234.14
8	181.31	227.96	272.75
32	217.37	278.17	339.88
128	244.66	316.71	392.84
512	270.65	353.32	445.64
1024	280.77	366.62	470.77
2048	289.83	384.32	487.43
4096	312.88	414.00	527.23

Temperature Coefficients

	35°–50°		50°–65°	
V	Cond. units	Per cent.	Cond. units	Per cent.
4	2.53	1.57	2.37	1.19
8	3.11	1.72	2.65	1.16
32	4.05	1.86	4.11	1.48
128	4.80	1.96	5.07	1.60
512	5.51	2.04	6.15	1.74
1024	5.72	2.04	6.94	1.89
2048	6.30	2.17	6.87	1.79
4096	6.74	2.15	7.55	1.82

Percentage Dissociation

V	35°	50°	65°
4	51.36	47.97	44.41
8	57.95	55.06	51.73
32	69.47	67.19	64.47
128	78.20	76.50	74.51
512	86.50	85.34	84.52
1024	89.74	88.56	89.29
2048	92.63	92.83	92.45
4096	100.00	100.00	100.00

Table XX.—Uranyl Nitrate, $UO_2(NO_3)_2.6H_2O$

Molecular Conductivity

v	35°	50°	65°
4	157.89	199.01	245.03
8	177.97	226.59	277.69
32	216.65	279.42	345.77
128	249.88	327.08	406.32
512	285.11	376.95	476.52
1024	304.61	404.71	514.08
2048	318.91	422.85	538.35
4096	349.78	467.92	596.77

Temperature Coefficients

	35°–50°		50°–65°	
v	Cond. units	Per cent.	Cond. units	Per cent.
4	2.74	1.74	3.07	1.54
8	3.24	1.82	3.41	1.50
32	4.18	1.93	4.42	1.58
128	5.15	2.06	5.28	1.61
512	6.12	2.15	6.64	1.76
1024	6.67	2.19	7.29	1.80
2048	6.93	2.17	7.70	1.82
4096	7.88	2.25	8.59	1.84

Percentage Dissociation

v	35°	50°	65°
4	45.14	42.53	41.06
8	50.88	48.42	46.53
32	61.94	59.72	57.94
128	71.44	69.90	68.09
512	81.51	80.56	79.85
1024	87.09	86.49	86.14
2048	91.17	90.37	90.21
4096	100.00	100.00	100.00

Table XXI.—Uranyl Sulphate, $UO_2SO_4.3H_2O$

Molecular Conductivity

V	35°	50°	65°
8	158.81	179.79	197.94
32	201.03	223.69	240.24
128	158.21	288.77	309.93
512	333.38	381.83	416.68
1024	377.29	436.95	488.19
2048	428.71	512.04	582.85
4096	484.32	597.28	694.01

Temperature Coefficients

	35°–50°		50°–65°	
V	Cond. units	Per cent.	Cond. units	Per cent.
8	1.40	0.88	1.21	0.67
32	1.51	0.75	1.10	0.49
128	2.04	0.79	1.41	0.49
512	3.23	0.97	2.32	0.61
1024	3.97	1.05	3.42	0.78
2048	5.49	1.28	4.72	0.92
4096	7.53	1.55	6.45	1.08

Percentage Dissociation

V	35°	50°	65°
8	32.79	30.10	28.52
32	41.51	37.45	34.62
128	53.31	48.35	44.66
512	68.83	63.93	60.04
1024	77.90	73.16	70.34
2048	88.52	85.73	83.98
4096	100.00	100.00	100.00

Table XXII.—Uranyl Acetate, $UO_2(C_2H_3O_2)_2.2H_2O$

Molecular Conductivity

V	35°	50°	65°
8	50.15	63.14	77.48
32	66.36	82.48	99.33
128	86.21	106.30	126.95
512	109.30	132.66	156.86
1024	119.64	144.10	170.74
2048	131.55	158.30	185.97
4096	151.69	183.60	216.99

Temperature Coefficients

	35°–50°		50°–65°	
V	Cond. units	Per cent.	Cond. units	Per cent.
8	0.87	1.73	0.97	1.54
32	1.07	1.61	1.12	1.36
128	1.34	1.55	1.38	1.30
512	1.56	1.42	1.61	1.21
1024	1.63	1.36	1.78	1.23
2048	1.78	1.35	1.84	1.16
4096	2.13	1.40	2.23	1.21

Percentage Dissociation

V	35°	50°	65°
8	33.1	34.4	35.7
32	43.8	44.9	45.8
128	56.8	58.9	58.5
512	72.1	72.3	72.3
1024	79.2	78.5	78.7
2048	86.7	86.2	85.7
4096	100.0	100.0	100.0

Table XXIII.—Hydrochloric Acid, HCl

The original solution, made by passing a calculated amount of hydrogen chloride gas into "conductivity" water, was standardized against a solution of alcoholic potash which had been standardized against potassium tetroxalate (kindly furnished me by Dr. H. O. Eyssell). The results agreed almost exactly with a determination of the chlorine gravimetrically as silver chloride.

Molecular Conductivity

V	35°	50°	65°
8	409.41	479.21	545.15
16	419.19	493.70	562.18
32	430.36	511.38	579.44
128	440.73	522.12	596.58
512	444.27	525.32	598.69
1024	434.68	510.79	585.20

Temperature Coefficients

	35°–50°		50°–65°	
V	Cond. units	Per cent.	Cond. units	Per cent.
8	4.65	1.14	4.40	1.92
16	4.97	1.19	4.57	0.93
32	5.40	1.25	4.54	0.89
128	5.43	1.23	4.96	0.95
512	5.43	1.22	4.89	0.93
1024	5.07	1.17	4.96	0.97

Percentage Dissociation

V	35°	50°	65°
8	92.15	91.22	91.06
16	94.35	93.98	93.90
32	96.87	97.35	96.78
128	99.20	99.39	99.65
512	100.00	100.00	100.00
1024	97.84	97.23	97.75

Table XXIV.—Nitric Acid, HNO_3

Standardized against the alcoholic potash which was used for hydrochloric acid (*q. v.*).

V	35°	50°	65°
4	366.32	428.63	472.54
8	386.08	454.51	511.18
16	399.13	466.54	529.08
32	412.37	486.24	553.20
128	421.25	499.17	569.97
512	425.26	503.90	577.82
1024	416.39	493.80	609.91

Temperature Coefficients

	35°–50°		50°–65°	
V	Cond. units	Per cent.	Cond. units	Per cent.
4	4.15	1.13	2.93	0.68
8	4.56	1.18	3.78	0.83
16	4.49	1.13	4.16	0.89
32	4.92	1.19	4.46	0.92
128	5.19	1.23	4.72	0.95
512	5.24	1.23	4.93	0.98
1024	5.16	1.24	7.74	1.57

Percentage Dissociation

V	35°	50°	65°
4	86.14	85.06	77.48
8	90.79	90.20	83.81
16	93.86	92.59	86.75
32	96.97	96.50	90.70
128	99.06	99.06	93.45
512	100.00	100.00	94.74
1024	97.91	97.99	100.00

Table XXV.—Sulphuric Acid, H_2SO_4

The acid was determined as barium sulphate.

Molecular Conductivity

V	35°	50°	65°
4	377.48	412.68	443.74
8	477.22	527.78	564.55
16	504.21	554.34	597.19
32	551.37	600.95	641.99
128	657.91	718.48	757.05
512	797.94	893.04	953.00
2048	862.33	998.08	1111.85
8192	892.55	1077.34	1203.92

Temperature Coefficients

	35°–50°		50°–65°	
V	Cond. units	Per cent.	Cond. units	Per cent.
4	2.35	0.62	2.07	0.50
8	3.37	0.71	2.45	0.46
16	3.34	0.61	2.86	0.52
32	3.31	0.60	2.74	0.46
128	4.04	0.61	2.57	0.36
512	6.34	0.79	4.00	0.45
2048	9.05	1.05	7.58	0.76
8192	12.32	1.17	8.44	0.78

Percentage Dissociation

V	35°	50°	65°
4	42.3	38.3	36.9
8	53.5	50.1	46.9
16	56.5	51.5	49.6
32	61.8	55.8	53.3
128	73.7	66.7	62.9
512	89.4	82.9	79.2
2048	96.6	92.6	92.4
8192	100.0	100.0	100.0

Jones and Caldwell,[1] Jones and MacKay[2] and Jones and Hosford[3] have shown by tables that the value for the molecular conductivity of an alum is less than that of the sum of its constituent salts, and that these differences are little affected by rise in temperature. The tables compiled by

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[1] This Journal, **25**, 349 (1901).

[2] *Ibid.*, **34**, 357 (1905).

[3] *Ibid.*, **46**, 240 (1911).

Hosford from earlier work done in this laboratory show further that the differences are smaller the greater the dilution. This is what would be expected since dissociation increases with dilution.

The complexities of the changes of the violet chrome alums into green varieties readily account for their irregularities, but there follow tables which show that in addition to ionization, there is a breaking down of the complex salts into simpler ones. The tables are compiled from the work of Drs. Winston[1] [$Cr_2(SO_4)_3$, $(NH_4)_2SO_4$, and Na_2SO_4], West[2] (K_2SO_4) and Hosford[3] ($NiSO_4$):

Table XXVI.—Conductivities of Complex Salts

Ammonium Chromium Sulphate

V	$Cr_2(SO_4)_3$	$(NH_4)_2SO_4$	Sum/2	$NH_4Cr(SO_4)_2$	Diff.
8	151	213	182	170	—12
32	230	255	242	229	—13
128	338	292	315	303	—12
512	472	313	392	410	+18
1024	562	323	442	483	+41
2048	708	337	522	577	+55

Potassium Nickel Sulphate

V	K_2SO_4	$NiSO_4$	Sum	$K_2Ni(SO_4)_2$	Diff.
8	220	93	313	273	—40
32	260	127	387	349	—38
128	297	172	469	432	—37
512	320	219	539	514	—25

Potassium Sodium Sulphate

V	K_2SO_4	Na_2SO_4	Sum/2	$KNaSO_4$	Diff.
8	220	178	199	200	+1.0
32	260	215	237.5	237	—0.5
128	297	247	272	270	—2.0
512	320	270	295	291	—4.0

Potassium Chromium Sulphate

V	$Cr_2(SO_4)_3$	K_2SO_4	Sum/2	$KCr(SO_4)_2$	Diff.
8	151	220	185	167	—18
32	230	260	245	226	—19
128	338	297	317	298	—19
512	472	320	395	404	+ 9

[1] THIS JOURNAL, **46**, 368 (1911).

[2] *Ibid.*, **34**, 357 (1905).

[3] *Loc. cit.*

Hydrolysis was noted in several instances and one salt, dipotassium phosphate, showed a time factor.

Jones and MacKay,[1] in their study of the alums, found that the conductivities for certain of the alums were not constant but changed with time. Some of their results are taken from the paper cited.

Sodium Aluminium Alum

V	Time	Molecular conductivity
20000	0	529
20000	24 hrs.	550
	Ammonium Chromium Alum	
2000	0	630
2000	24 hrs.	686
	Ammonium Iron Alum	
200	0	320
200	2 hrs.	330
400	0	411
400	20 min.	424
2000	0 min.	694
2000	30 min.	808
2000	18 hrs.	891
2000	21 hrs.	896

When we made our measurements with dipotassium phosphate they were found not to agree with those of Miss Winston, and were therefore repeated a week later, when it was found that there was still greater disagreement. At about this time some of the cells were sent away for repairs and it was three weeks before the work could again be repeated. The same mother solution was used and, as the next table shows, for concentrated solutions the variation was again increased. The table shows two things. First, the time factor for hydrolysis is greater for concentrated than for dilute solutions. Second, the temperature has little effect on the time factor. According to the law of mass action, the first would be expected. It is, however, undoubtedly true that a cause of the discrepancies between this work and the earlier work is accounted for in the time required for the hydrolysis equilibrium of the salt.

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[1] This Journal, **19**, 105 (1897).

Table XXVII.—Molecular Conductivities of Dipotassium Phosphate

Column I. Jones and Winston[1]
Column II. From readings made November 22
Column III. From readings made November 28
Column IV. From readings made December 22

	35°			
V	I	II	III	IV
2	138	140	187	198
8	175	184	307	316
32	204	222	332	334
128	230	252		372
512	240	290	420	414
1024	243	276	427	426
2048	243	268	424	422
4096	251	265	424	

	50°			
V	I	II	III	IV
2		175	233	247
8		234	387	401
32		286	422	428
128		322	491	479
512		346	541	533
1024		348	550	545
2048		345	546	545
4096		340	544	

The salts brought within the range of this investigation crystallizing with the largest number of molecules of water are sodium ferrocyanide, $Na_4Fe(CN)_6.12H_2O$, potassium chromium sulphate, $KCr(SO_4)_2.12H_2O$, potassium nickel sulphate, $K_2Ni(SO_4)_2.6H_2O$, and ammonium chromium sulphate, $NH_4Cr(SO_4)_2.12H_2O$. These salts have the largest temperature coefficients of any of those studied, and at the highest dilutions and temperatures vary between eleven and eighteen conductivity units for each degree. Furthermore, for every salt that did not undergo hydrolysis, the temperature coefficients increased with dilution up to infinite dilution, that is, up to that dilution which showed the greatest molecular conductivity.

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[1] *Loc. cit.*

When hydrolysis takes place the temperature coefficients do not increase so regularly with dilution, although, in general, these coefficients become larger with increased dilution. These observations agree with those previously published.[1]

Hosford and Jones[2] have shown that while the violet variety of ammonium chrome alum has a smaller conductivity than the green in more concentrated solutions, in the more dilute the green has the smaller conductivity, the change taking place between $V = 1024$ and $V = 2048$. This is true at lower temperatures. At higher temperatures the values for both the green and the violet varieties are more nearly equal, due probably to a gradual transformation of the violet into the green variety (see Jones and MacKay[3]).

Monti,[4] Recoura[5] and Whitney[6] have studied the nature of the transformation of the violet chromium sulphate into the green, and undoubtedly the same changes take place in the presence of ammonium and potassium sulphates, that is, in solutions of the alums.

Whatever the interpretation, there is no doubt that a complex ion is formed, made up of SO_4 and Cr. This does not separate into the chromium or sulphuric acid ions, since ammonia will not precipitate all the chromium nor barium chloride all the sulphuric acid. The measurements show that the sum of the conductivities of this complex ion and such others as may be formed is greater than that for the ions from the violet chromium sulphate or the alum.

After the conductivities of potassium permanganate had been measured the cells were found to have been stained brown with manganese dioxide. As the mother solution had been heated to 50°, undoubtedly there was greater decomposition than would have appeared had the solutions been made up originally at, say, 20°. This will account for the lower values obtained at higher temperatures.

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[1] Jones: This Journal, **35**, 450 (1906).

[2] *Loc. cit.*

[3] This Journal, **19**, 103 (1897).

[4] Z. anorg. Chem., **12**, 75 (1896).

[5] Ann. chim. phys., [7] **4**, 494 (1895).

[6] Z. physik. Chem., **20**, 40 (1896).

The four salts of uranyl that were studied underwent more or less hydrolysis, and therefore agreement was not found with previous workers. Miss Winston[1] observed an increase in percentage dissociation with rise of temperature for uranyl acetate, and attributed the large dissociation to induction. If, as seems possible, there is always a time factor for hydrolysis, this factor would be greater for concentrated than for dilute solutions.

In uranyl acetate the dissociation is greater for higher temperatures only with greater concentrations.

The first table for dipotassium phosphate shows dissociation percentages greater at higher temperatures, but in the second the decrease is seen to be about normal. These measurements, taken, the second a month after the first, show that the greater the interval of time the lower the percentage dissociation. Hence dissociation when measured before hydrolysis is complete does not give concordant results because the more concentrated solutions are less hydrolyzed than the more dilute.

SUMMARY

1. The molecular conductivities have been measured and the temperature coefficients and percentage dissociation calculated for the following salts and acids: Sodium ferrocyanide, potassium carbonate, potassium permanganate, dipotassium phosphate, potassium sodium sulphate, potassium chromium sulphate (violet and green), potassium nickel sulphate, ammonium chromium sulphate (violet and green), calcium bromide, calcium chromate, zinc nitrate, zinc acetate, lead chloride, lead acetate, nickel acetate, uranyl chloride, uranyl nitrate, uranyl sulphate, uranyl acetate, hydrochloric acid, nitric acid and sulphuric acid.

2. Double salts in general have smaller conductivities than the sums of the conductivities of the constituent salts. These differences are little affected by temperature but become less with greater dilution.

3. Certain apparent discrepancies between this work and that of other workers are explained: 1. By hydrolysis with time

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[1] *Loc. cit.*

factor. 2. By decomposition such that new substances are formed.

4. The observations of previous workers as to large temperature coefficients for salts that crystallize with large amounts of water were confirmed. For salts that did not undergo hydrolysis the temperature coefficients increased with dilution.

5. The violet varieties of ammonium and potassium chrome alum have smaller conductivities than the green varieties, but the differences become less at higher temperatures.

6. Hydrolysis was noticed in several instances. One salt, dipotassium hydrogen phosphate, had a time factor which extended over days or even weeks.

7. With the exception of uranyl acetate and dipotassium hydrogen phosphate, there was a decrease in percentage dissociation with rise in temperature. After standing four weeks the phosphate acted normally.

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JOHNS HOPKINS UNIVERSITY
May, 1912

REPORT

THE MOLECULAR THEORY[1]

There are few doctrines which are of as great interest, from the historical point of view, as the molecular theory. Promulgated in ancient times by Leucippus and Democritus, it has, at different times, passed through the most varying stages; it has been considered as certain truth, it has been scorned as a grossly materialistic picture. Leucippus professed the doctrine that matter consists of indivisible and indestructible atoms which move in space. Democritus held the same views. All phenomena depend upon the collision, the contact and the separation of the atoms. They are of different shapes and sizes.

These ideas were violently combatted by the school of idealistic philosophers at Athens, of Plato and Aristotle, afterwards regarded as the great masters of science; as a matter of fact, they enormously impeded by their doctrines, as has been observed by Berthelot, the progress of chemistry. Nevertheless, at the beginning of modern times we find in Gassendi, in Descartes and in Newton practically the same ideas as those of Democritus. Modern chemistry had not yet been born. All sorts of shapes, sizes and movements were attributed to the atoms, which persisted only as a rather ingenuous philosophical conception. It was reserved for Dalton to give a chemical bearing to the atomistic doctrine. To him the movement of the atoms was of secondary interest. This physical part of the atomic hypothesis was developed by Daniel Bernouilli in an interesting memoir (in 1738) which contains the nucleus of the kinetic theory of gases. Descartes had already expressed the opinion that heat results from the movement of the corpuscular particles. Bernouilli put forth the same opinion in a more precise manner. According to him, the quantity of heat contained in air is proportional to its elasticity.

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[1] One of a series of addresses made at the University of Paris from March 6 to 13, 1911, and published by A. Hermann & Fils; see Book Reviews, THIS JOURNAL, 48, 548

But the great period in the development of the atomistic, or, rather, molecular idea came only after the introduction of the mechanical theory of heat in the middle of the last century. The great masters of this theory, Joule, Clausius, Maxwell, derived with marvelous success, by ingenious calculation, a large number of the properties of gases from their movement. Mention must also be made of Waterston, who, in 1845, twelve years before Clausius, gave a detailed theory of the properties of gases, which, however, was forgotten and brought to light by Lord Rayleigh about half a century later.

The authority of the propounders of the theory, so natural and so attractive that it had already suggested itself to the philosophers of antiquity, was so great that the theory was regarded as an integral part of thermodynamics, the superb creation of the immortal Sadi Carnot; it was regarded, then, as the pure truth. On the other hand, chemists were determining the relative positions of the atoms in the molecules and constructing formulas giving, as it were, the whole topography of the molecules. Opponents were not lacking, as, for example, the somewhat fiery genius of Kolbe, but at last the victory became complete and triumphed in the construction of chemical formulas in space by van't Hoff and Le Bel. Still wider became the extent of this theory when van't Hoff proposed the hypothesis, which has since proved so fertile, that dissolved substances possess all the properties of gases, a hypothesis the first traces of which are found developed in a memoir by Gay-Lussac (1839), who, however, did not consider the quantitative side of the question.

Van't Hoff was in fact an atomist, but a very cautious one. He said that he did not wish to connect his hypothesis with that of the movement of the molecules, proposed by the partisans of the kinetic theory of gases. Nevertheless, the physical chemists who accepted his views followed, in general, this natural road, and Boltzmann and van der Waals declared themselves in favor of the kinetic interpretation of the facts brought out by van't Hoff. At this point, a pronounced reaction was felt. In fact, a large number of the properties of matter could be deduced, without recourse to a kinetic representation, by means of the so-called thermodynamic method developed by Willard Gibbs, Helmholtz, Planck, Duhem, and other masters of modern physical theory. The kinetic theory was, in truth, not very easy to manipulate and for this reason lost a great part of its utility. Boltzmann revived it by reducing it to an application of the theory of probabilities, and this theory found an elegant application in the deduction of the laws of radiation.

Nevertheless, chemists were comparatively insensible of this remarkable progress. The theory claimed to be able to calculate the size of the molecules, but the calculation was quite indirect and led to results which differed considerably, varying from two to one hundred trillions of molecules in a gaseous mass of one cubic centimeter at 0° and atmospheric pressure. The most probable number was about twenty trillions (10^{18}). At this period a reaction was felt. Wald, a Czech philosopher and theorist, published a philosophical analysis on the true significance of the laws of Dalton concerning the constant composition and multiple proportions in the composition of chemical products. He expressed the opinion that industrial products have a constant composition because the manufacturers consider constant composition as a sign of purity and consequently treat their products until they show that constancy. The objection that the products of nature also possess, in general, a constant composition was met by the assertion that nature works in about the same way as the manufacturers, especially in the way of recrystallizations.

This idea would probably not have had much success if there had not existed another tendency, which made itself felt at the same period, of purging thermodynamics as much as possible of every trace of accessory hypotheses. A new exposition of the scientific results in this domain was made in accordance with a method which we call that of energetics. The central theorem of this doctrine of energetics, inaugurated by Helm in 1887, is that every quantity of energy is the product of two factors, one called intensity (or potential), the other capacity.

Ostwald accepted these ideas, which he chose as the basis of his exposition of thermodynamics (*Treatise on General Chemistry*, Vol. II, Leipzig, 1893). But the greatest sensation was produced by an address made by Ostwald at the meeting of the German naturalists at Lubeck, in 1895, on the "Demolition of Scientific Materialism." A large number of idealistic philosophers and theologians were attracted by the sensational title and hastened to support this movement. Boltzman, on the other hand, wrote a satirical and decisive criticism in the *Annalen der Physik.*

But Ostwald did not surrender so easily. Called to London to make one of the addresses in memory of Faraday, he showed to the astonished audience, who had hoped to learn something on catalytic phenomena, that the laws of Dalton could be explained without the aid of the molecular theory (1904).

At this time, the first investigations on the limit of the electrical charge, already carried out on quite a large scale by Sir J. J. Thomson and his students, Townsend and Wilson, had led to a value of about 3×10^{-10} electrostatic units. Planck, in 1901, had published his important theoretical calculations which led to a value of 4.7×10^{-10} electrostatic units. This agreement was of an entirely different order from that which had been obtained by means of the kinetic theory of gases. This value corresponds to a number $N = 43 \times 10^{18}$ per cc. or $N = 963{,}000 \times 10^{18}$ per gram molecule, which agrees fairly well with the average number of about 20×10^{18} for the number of molecules in a cubic centimeter under normal conditions, as previously found. It is this absolutely independent determination which completely overcame the opposition to the molecular theory. This road, so full of promise, was followed further and you see in the table below the different values which have been found. You will perhaps especially admire the work of Rutherford and Geiger in England and that of Regener in Germany, who counted the number of α particles emitted by a radioactive preparation by counting the number of scintillations which they produced on a zinc sulphide screen. An electrometer gave the corresponding quantity of electricity. The electrical charge of each α particle was, in fact, found to be double that written in the table, which coincides almost absolutely with the theoretical value given by Planck. It was supposed, therefore, that the α particle consists of an atom of helium, carrying two unit charges like a bivalent ion, such as Ca or Ba; this assertion is quite natural, since helium has a valence of zero and valence generally changes in even numbers; consequently, the unstable ionized helium must have an electrical charge of two units. You see how little the different determinations made during the years 1908 and 1909 vary from the mean, 4.54. It was therefore thought to be absolutely sure that the truth had been found.

		Minimum charge $e \times 10^{10}$	
H. v. Helmholtz, Richarz	1890	1.29	
H. A. Lorentz, C. J. Stoney	1890	1.29–6.1	
J. S. Townsend	1898	1.2–1.5	
R. F. Lattey	(1909)	5	
J. J. Thomson	1898–99	6.5–6.8	(6.0–8.4)
M. Planck	1901	4.69	
E. Bauer, M. Moulin	(1909)	5.55	
J. Nabl	1902	2	
J. J. Thomson	1903	3.4	(3.3–3.5)
H. A. Wilson	1903	3.1	(2.0–4.4)
H. Pellat	1907	2.46–6.9	
K. Przibram	1907	3.8	(1.7–6.2)
R. H. Millikan, L. Begeman	1908	4.03	(3.66–4.37)
E. Rutherford, H. Geiger	1908	4.65	(4.15–5.5)
E. Regener	1908	4.79	
R. Tabor, R. F. Lattey	1909	4.47	(3.13–5.74)
A. Alexeiew, M. Malikow	1909	4.5	(3.0–6.3)
F. Ehrenhaft	1909	4.46–4.68	
G. Moreau	1909	4.3	(4.1–4.8)
M. de Broglie	1909	4.5	
J. Perrin	1909	4.11, 4.05, 4.50	
R. A. Millikan	1910	4.66	
F. Ehrenhaft	1910	0.8–12.4	(Pt)
		0.9–26.7	(Ag)
		0.5–9.6	(Au)
		0.5–28.9	(P)
K. Przibram	1910	3.45	(O)
		4.2	(Air)
		4.15	(HCl)
		4.7	(P)

Fortunately, another method, different from the electrical method, was found. This was the Brownian movement, which, from the investigations of Regnauld, Wiener, Exner, Renard and Gouy, had been found to conform so closely to the supposed movement of the molecules that it was called the molecular Brownian movement. This movement of little particles of the order of magnitude of 0.001 millimeter had been discovered by an English botanist, R. Brown (1827). The study of it was taken up again during the last five years, when the interest in colloidal solutions rose to a high degree, and when the ultramicroscope had been constructed for the observation of small particles which are not visible with the ordinary microscope. The theory of this movement was put forth by Einstein and de Smoluchowski. Svedberg showed that this movement is of the order of magnitude which is demanded by the kinetic theory for molecules of the size of the particles observed.

This discovery made such a great impression on Ostwald that he conceded that, after all, matter is not continuous but divided into distinct particles which correspond to the molecules.

But it was reserved for Perrin[1] to draw extremely important conclusions from a deep study of the properties of these little particles. You are without doubt familiar with that masterly work, carried out with "Gallic elegance," which wins the admiration of every one. The distribution of the particles under the influence of weight—analogous to the increase in the density of the air from the upper to the lower part of the atmosphere—gave him a value of N equal to 70.5×10^{22} for a gram molecule. The Brownian movement itself gave the very nearly equal number 71.5×10^{22} and finally he was able to determine N by means of the rotation of the little particles, using a formula of Einstein's. In this way he found $N = 65 \times 10^{22}$. These three determinations give the value of N which is at present the most trustworthy—and since the recent experiments of Ehrenhaft and Przibram we can congratulate ourselves on having these direct measurements of the movement of the molecules.

There is still another determination in this field which I consider as being of rare importance. We know now, thanks to the work of Perrin, that suspended particles behave in the same way as the kinetic theory requires of gas molecules. The molecules of solutions probably move in an analogous manner, but, as we have just seen, van't Hoff did not wish to connect his theory of dilute solutions with so uncertain a hypothesis. Fortunately, Svedberg has filled in this gap. We know that molecular transformations do not proceed uniformly. This is true also of the emission of α particles.

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[1] See articles of Jean Perrin in the *Revue du mois:* La discontinuité de la matière, Vol. **1**, p. 323; Peut-on peser un atome avec précision? Vol. **6**, p. 513

Regener had verified a formula deduced from the theory of probabilities by von Schweidler, who found that the relative variation d (in percentage) from the mean number n per second is inversely proportional to $\sqrt{n}$. Svedberg repeated the determination with a sample of polonium precipitated on a plate of copper and found $d = 42.3$ per cent. instead of 42.8 per cent. calculated according to von Schweidler's formula, n being 0.559 per second.

Then, he reasoned as follows: In a given volume of a solution, the number of molecules of dissolved substance is not constant on account of the molecular movement. De Smoluchowski has given a formula which makes it possible to calculate, in percentage of the mean number, the deviation d_1 due to this cause. If, now, a radioactive salt, such as polonium chloride, is dissolved in water and if the number of α particles produced per second is observed, the observed number must deviate by a certain amount D from the mean number n, and this deviation must be $D = \sqrt{d^2 + d_1^2}$, where d and d_1 are the deviations calculated from the formulas of von Schweidler and de Smoluchowski. He found the following values:

n =	0.476	0.349	0.224	particles per second
$D_{\text{obs.}}$ =	55.3	71.5	83.4	per cent.
$D_{\text{calc.}}$ =	58.6	68.8	80.5	per cent.
$d_{\text{calc.}}$ =	46.4	54.1	67.6	per cent.

The observation was carried out in such a way that a drop of a solution of polonium chloride was placed under a transparent screen covered with zinc sulphide, which was examined under a microscope. The α particles are emitted from a portion of the solution which has a depth of 0.05 millimeter. The drop is much larger and, consequently, the formula of de Smoluchowski is applicable.

The agreement of the calculated numbers D with the observed numbers is very satisfactory. On the other hand, the difference between D and d, which would hold for immobile molecules (fixed on a copper plate, for example), is sufficiently great to permit of concluding with certitude that the dissolved molecules (here probably the ions) move as demanded by the kinetic theory.

From this, it does not seem possible to doubt that the molecular theory, glimpsed by the philosophers of antiquity, by a Leucippus, by a Democritus, hit the truth, at least in its essential parts.

But let us return now to the determination of the minimum electrical charge. All the measurements made before 1910 are based on the means taken on a large number of particles. Either the movement of a fog consisting of a large number of particles or the total charge of a large number of α particles was measured, or the movement of simple particles was determined in an electrical field and the charge of this particle was calculated. The isolated measurements were then collected into a mean holding for a large number (Ehrenhaft, de Broglie).

Millikan published isolated values for charged drops falling in an electrical field. He found that the charge varied between the wide limits 8.6×10^{-10} and 29.8×10^{-10}. He collected the values into groups; in a first group, the double minimum charge varied from 8.6 to 10.1; in another, the triple charge varied from 13.5 to 14; in a third, the quadruple charge varied from 17.5 to 19.1. The quintuple charges varied from 22.5 to 24.5; the sextuple charge from 26.9 to 28.8. There are evidently certain charges which are more frequent and are multiples of the minimum charge, which he determined to be 4.66×10^{-10}. However, the groups are not very distinct and for this reason Ehrenhaft has very severely criticized the conclusions of Millikan.

These investigations were carried out on a much larger scale by Ehrenhaft and Przibram, at Vienna, who made several thousand experiments. Ehrenhaft found, on excluding those values which were so small that their reality might be doubted, the following numbers for small metallic particles produced by evaporation in the electric arc or for droplets formed in moist air in contact with yellow phosphorus:

For platinum, minimum charge	0.9 to	12.4
silver	0.9	26.7
gold	0.5	9.6
phosphorus	0.5	28.9

There were, therefore, charges very much lower than those calculated from the mean values; the minimum charge of a separate particle may be but one-fifth (0.9×10^{-10}) that (4.5×10^{-10}) which is regarded as the most probable from the earlier measurements. There are all kinds of charges from this minimum up to six times the mean minimum charge.

Ehrenhaft was very much surprised at the results of his measurements, which seemed incompatible with the large number of determinations made before, to which he himself had contributed and which give results agreeing marvelously with the theoretical value 4.69×10^{-10} calculated by Planck. A new difficulty seemed to arise here. Some authors recalculated, from new determinations of the radiation constants, Planck's value, which was somewhat higher than the mean experimental value, and found $e = 5.55 \times 10^{-10}$, i. e., 18 per cent. higher. Later, however, it was found that the number given by Planck is correct.

Ehrenhaft then asked his friend, Przibram, who had also previously contributed to the determination of the minimum charge and found a number about 20 per cent. too small, to carry out new measurements on a still larger scale. Przibram performed this work with an extraordinary assiduity. Just for the particles formed in moist air in contact with phosphorus, he made more than a thousand determinations. He found charges varying from about 0.7×10^{-10} to 190×10^{-10}. The frequency of the charges showed maxima and minima. Taking the difference of the charges for two consecutive maxima or minima, he determined the mean minimum charge and found the following values for charged particles, prepared in the manner indicated:

Particles suspended in electrolytic oxygen	$e = 3.45 \times 10^{-10}$
Particles suspended in air through which electrical discharges were passed	$e = 4.7 \times 10^{-10}$
Particles suspended in fogs of hydrochloric acid[1]	$e = 4.15 \times 10^{-10}$
Particles suspended in air, in contact with yellow phosphorus	$e = 4.7 \times 10^{-10}$

It must be acknowledged that the maxima and minima were not equidistant, as is shown by the figures published by Przibram.

A criticism of Ehrenhaft shows that the groups of Millikan are not distinct, but overlap each other, so that the means are quite subjective. Everything seems to show, then, that the minimum value is but a mean. The numbers of Przibram agree very well with those of Perrin, as shown by the table above.

Series of different experiments, carried out at different times with yellow phosphorus, do not give the same value for *e;* it varies from about 3×10^{-10} to 7×10^{-10}; it is only the mean which gives the number 4.7×10^{-10} and which agrees fairly well with that found by other authors.

The great success obtained by the first determinations of the minimum charge led Planck to develop a theory of radiation, according to which radiant energy is also composed of small equal quantities, which, however, vary with the wave length. This theory seems to be confirmed by some experiments of Stark and Ladenburg. Yet Sir J. J. Thomson, with his great authority, has taken a stand against this opinion which, in fact, it is somewhat difficult to admit, and he has given another explanation of the results of Ladenburg. The difficulties in regard to the minimum electrical charge necessarily increase those of introducing the notion of a minimum energy. We must follow with the greatest interest the development of these ideas which are evidently but at their beginning.

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[1] Charged by means of radium, otherwise this fog is not charged.

What must we now conclude from the large number of experiments in this field? The kinetic theory of gaseous or liquid matter is evidently established beyond doubt. The great masters, Joule, Clausius, Maxwell and Boltzmann, not to mention Leucippus and Democritus, have found a new confirmation of their divinatory power. It has also been possible, it seems, to ascertain that the mean electrical charge of particles and also of ions is constant and about 4.5×10^{-10} electrostatic units. But this seems to be true only for a very large number of particles or ions. The individual charge varies between quite wide limits. Consequently, it seems probable that a molecule of sodium chloride,. which consists of quantities of sodium and chlorine charged with equal quantities of electricity of opposite signs, has not the same composition as another molecule of this salt, but that, if we take a large number of these molecules, the mean composition is constant.

Another hypothesis, according to which all the molecules of a salt would have the same composition but some of them charged positively, others negatively, so that the total charge would be zero, is not admissible.

We would, in fact, in this manner come to the conclusion that not only the ions, but the nondissociated salt also, carried the electricity in the electrolyte. The latter transport of electricity would be similar to metallic conductivity. It would be necessary to make a new hypothesis to explain how it is possible that this conduction without electrolysis can never be detected, and this hypothesis would consist in that there is always proportionality between the conductivity due to the ions and that due to the molecules. Such a hypothesis is extremely artificial and must hence be discarded.[1]

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[1] In a memoir dated April, 1911, Millikan has subjected the determinations of Ehrenhaft and Przibram to detailed criticism. Millikan finds, for the minimum charge of droplets of oil or of mercury, $e = 4.9 \times 10^{-10}$ electrostatic units. Somewhat later, Perrin (*Compt. rend.*, **152**, 1165) found that the currents produced within the interior of the droplets used introduce into the experiments of Millikan a

Science advances very rapidly in our day. No chapter of physical chemical science can give a better proof of it than the atomistic theory. We might be tempted to conclude from it that our ideas on scientific problems are of extremely little value, since they change from day to day. Nothing could be more erroneous. The theoretical ideas of Dalton were very much superior to those of the philosophers of antiquity. The superiority consisted in the quantitative element of these laws, which could be verified in a very exact manner. In fact, they also serve as the solid foundation of the development of scientific chemistry since his time. The kinetic theory contributed to a very high degree in giving us a simple representation of the heat energy of matter; in physical chemistry it explained the very important law of Avogadro and that of van't Hoff. The determination of the molecular electrical charge and still more the study of the Brownian movement secured the triumph of the kinetic theory against the attacks of the school of energetics. The deep study of the electrical charge of suspended particles seemed to make probable the fact that the chemical law of the constant composition of chemical products is only a statistical law holding for a large number of molecules. In the same way Avogadro's law, according to which the active force of molecules is proportional to the temperature and independent of the composition of the molecules, does not hold for every individual molecule but only as a mean for a large number of molecules.

The last measurements of Millikan, of Perrin and of his students have still further corrected this irregularity; by establishing the constancy of the minimum charge, they have established that of the chemical composition of each individual molecule.[1]

The aspect has varied rapidly lately, but our conception as to the nature of matter has deepened enormously.

Over the kinetic-molecular theory we can write the motto of this superb city, *Fluctuat nec mergitur*. But the fluctuations diminish more and more and the rapid progress becomes more and more continuous and regular.

Svante Arrhenius

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source of error. He, himself, has given the value $e = 4.24 \times 10^{-10}$ electrostatic units. J. Roux has repeated the experiments of Millikan with droplets of sulphur, which may be considered as being solid, and has found $e = 4.17 \times 10^{-10}$ (*Loc. cit.*, p. 1168). Finally, Perrin made new determinations by his own methods and found $e = 4.2 \times 10^{-10}$ electrostatic units. This value must be considered as the most probable (*Compt. rend.*, **152**, 1380 and 1569). According to these new measurements, the minimum charge really seems to be constant.

[1] See the preceding note, p. 546.

OBITUARY

MORRIS LOEB

Morris Loeb, the well known chemist of New York City, died October 8, 1912, at the age of only 49, having been born in Cincinnati May 23, 1863. He was an alumnus of Harvard (class of 1883) and received his Doctor's degree at Berlin in 1887. The following year he spent at the Universities of Heidelberg and Leipzig. On his return to America, he acted as assistant to Prof. Wolcott Gibbs at Newport, Rhode Island, for one year, and from 1889 to 1891 he was docent at Clark University. From 1891 to 1906 he occupied the chair of chemistry at New York University, being made director of the chemical laboratory in 1895.

Dr. Loeb was a man of wealth and many interests, but even after he abandoned his educational work, his love of science did not wane. He was a member of numerous scientific societies and an officer of many of them. He made unstinted use of his talents and wealth in furthering the interests of art and music, in charities and social service work. To him more than any other one man, perhaps, the Chemists' Club of New York owes its present influential position among the chemists of America and its beautiful club house. The entire furnishings of Rumford Hall, of the Priestley Room, of the Library and Museum, were at his expense. In this building he kept a private laboratory and here he loved to spend what little time his numerous activities left him. At the time of his death he was serving his second term as president of the Club, and at a meeting of the Trustees, held Oct. 8, 1912, it was ordered that the following preamble and resolution be filed:

WHEREAS, Morris Loeb, the President of the Club, has been taken from us by death, and

WHEREAS, He was the leading spirit in bringing to fulfilment ambitions and plans that had long been ours, and

WHEREAS, He was always ready to shoulder burdens and to give help, and

WHEREAS, He was a man of order, and of integrity, in mind and heart, sincere in scholarship, living without malice or scorn, speaking no evil, and generous in judgment, and

WHEREAS, We were drawn to him by ties of deep and abiding affection, now, therefore, be it

Resolved, That we make this minute of our poignant grief at his passing, and that we cherish his memory as another of his great gifts to science and to humanity.

ELLWOOD HENDRICK
CLIFFORD RICHARDSON
WALTER E. ROWLEY
Committee

REVIEWS

CONFÉRENCES SUR QUELQUES THÈMES CHOISIS DE LA CHIMIE PURE ET APPLIQUÉE, faites à l'Université de Paris du 6 au 13 mars, 1911, par SVANTE ARRHENIUS, Directeur de l'Institut Nobel scientifique, à Stockholm. Paris: Librairie Scientifique A. Hermann et Fils. 1912. pp. 112. Price, Fr. 3.

The titles of the five lectures contained in this little book are as follows: The Molecular Theory; Suspensions and the Phenomena of Absorption; Free Energy; The Atmospheres of the Planets; The Physical Conditions of the Planet Mars. Anything which Arrhenius has to say is sure to be of interest and this is especially true of the present series of addresses, as they contain brief, but authoritative and lucid summaries of our knowledge on the subjects treated. A translation of the first lecture will be found on p. 536 of THIS JOURNAL.

C. A. R.

THEORETICAL AND PHYSICAL CHEMISTRY. By S. LAWRENCE BIGELOW, PH.D., Professor of General and Physical Chemistry in the University of Michigan. New York: The Century Co. 1912. pp. xiii + 544. Price, $3.

With text-books it is as with living organisms, the fittest survives. However much the author may feel called on to apologize for introducing a new competitor into the field, he will meet few complaints if he succeeds in producing a book which either collects together more scientific facts of a fundamental character than existing books, more aptly summarizes facts already known, throws new and suggestive light on obscure points, or gives a better digested pedagogical presentation of the most essential facts and principles of his subject. The last, at any rate, the present work may well claim to do. Physical chemistry is admittedly as difficult, as it is important, to teach thoroughly to students still in their earlier courses, and this admirable book will be very welcome to those who have found the classical German works too difficult for their purpose, and have not found a work in English which satisfied their requirements of comprehensiveness and simplicity, combined with scientific soundness of treatment. While the style at times shows evidences of hasty writing, and the choice of colloquially worded summaries as headings of paragraphs may not please all tastes, the author must be admitted to have a thorough comprehension of the limitations of the average student's mind, and of what will fix things in his memory. The subject matter is well chosen, no small thing in itself where the accumulation of detail is so enormous, and important theoretical deductions, mathematical or otherwise, are not neglected; though one misses the clear sequence of one fundamental theoretical principle, as, e. g., the theory of free energy in a well known German work. The style at times seems rather disconnected from sentence to sentence. Recent advances, such as the subject of radioactivity, are well summarized and chapters are given on the theory of inorganic evolution, and the luminiferous ether, etc. Even the theory of relativity comes in for a couple of pages, in this case unfortunately, since the author, in his rather contemptuous dismissal of its claims, betrays the fact that he has entirely failed to grasp what those clains are.

If criticism may be allowed where so much is admirable, the reviewer would suggest that, in a future edition, a little more attention should be given to precision of statement, especially on physical matters. Calories are not "quantity factors" in heat energy (p. 25) comparable to volume in the product *pv*, but are units of energy itself; the "gravitation constant" (p. 29) usually means the Newtonian constant, something quite different from the acceleration of gravity; on p. 31, line 4, "unit of mass" should be replaced by "gram;" and the statement relative to the kinetic theory of gases (p. 141) that "We may picture this to ourselves and realize that it must be so," etc., will hardly pass for proof of the identity of mean kinetic energy in two systems of molecules in equilibrium, since the same "reasoning" might just as well be applied to the momentum.

B. B. TURNER

SPECTROSCOPY. By E. C. C. BALY, F.R.S., Grant Professor of Inorganic Chemistry in the University of Liverpool, Fellow of University College, London. With 180 Illustrations. New Edition. Text-books of Physical Chemistry, Edited by SIR WILLIAM RAMSAY, K.C.B., F.R.S. London, New York, Bombay and Calcutta: Longmans, Green & Co. 1912. pp. xiv + 687. Price, 12 s. 6 d.

The first edition of this book appeared in 1905 and gave "typical investigations" of research work from its practical side. The second edition gives "a résumé of the salient points of the more modern work," thus making the book thoroughly up-to-date.

The first two chapters are historical and include a brief description of the work of Kirchoff, Angström, Rowland and Michelson. The chapters on "The Slit, Prisms and Lenses," "The Complete Prism Spectroscope," "The Prism Spectroscope in Practice," "The Diffraction Grating," and "The Ruled Grating in Practice," have remained practically unchanged in the second edition, only a few pages being added.

Considerable new material has been added to Chapter 8 on "The Extreme Infrared and Ultraviolet Regions of the Spectrum." This includes a description of radiomicrometers, thermopiles, bolometers, the focal isolation of heat waves, etc. As it seems probable that the infrared is an extremely fertile region for research, the author should have treated the infrared in a more detailed and thorough manner. Energy measurements in this region should be made in absolute units and the treatment of this subject should show how this can be done. It seems that our present knowledge of infrared emission and absorption spectra could have been given much more "saliently" than has been done. The ultraviolet is treated more satisfactorily. It does not include any discussion of the ionizing properties of ultraviolet light. To many this would seem proper in a text-book on spectroscopy.

The chapters on "The Application of Interference Methods to Spectroscopy," "The Practical Resolving Power of the Spectroscope," and "The Photography of the Spectrum," have been changed but little. The chapter on "Methods of Illumination" is improperly named as it includes the work of Schuster, Hemsalech, Schenck, Royds, Milner, Mohler, etc., upon the nature of the spark discharge. The chapter does contain many examples of sources of illumination and includes much new material. The chapter on "Phosphorescence and Fluorescence" is very short. It does not describe the very important work that has recently been done by Wood and others on the fluorescence of gases. The treatment of "Absorption Spectra" is necessarily incomplete on account of the enormous amount of uncorrelated material published. The absorption of organic compounds is given considerable space, whereas inorganic compounds are hardly mentioned.

The succeeding chapters are devoted largely to phenomena that have great theoretical importance. Remarkable as has been the development of our knowledge of spectra, yet chapters such as "The Nature of Spectra," "The Zeeman Effect," "Series of Lines in Spectra" and "Changes of Wave Length" have required but little change. The work on the Zeeman effect of absorbing substances at low temperatures, canal rays and the breaking up of fluorescent spectra into series lines should have been emphasized to a greater extent.

On the whole, the book is well written, though it does possess a compilation tone at times. It contains an enormous amount of information for a book of its size and, considering the unorganized nature of our spectroscopic knowledge at present, the author succeeds very well in giving us the more important part of the science. All students of experimental spectroscopy who cannot afford the luxury of owning Kayser's Handbuch should have Baly's Spectroscopy in their library. W. W. STRONG

ÜBER NEUE THERMODYNAMISCHE THEORIEN (Nernstsches Wärmetheorem und Quantenhypothese). Vortrag gehalten am 16. Dezember, 1911, in der Deutschen Chemischen Gesellschaft in Berlin von DR. MAX PLANCK, Professor der theoretischen Physik an der Universität Berlin. Leipzig: Akademische Verlagsgesellschaft m. b. H. 1912. pp. 34. Price, M. 1.50.

Planck gives a brief sketch of the development of thermodynamics, and then takes up the Nernst theory, which he defines as follows: "The entropy of a condensed, chemically homogeneous substance at absolute zero is zero."

He points out that this principle is not only important from the standpoint of chemically homogeneous substances but also for mixtures and solutions, and here is its important bearing upon chemistry. For details the lecture itself must be read. H. C. J.

DIE ENTDECKUNG DES RADIUMS. Rede gehalten am 11. Dezember, 1911, in Stockholm bei Empfang des Nobelpreises für Chemie, von MME. P. CURIE. Autorisierte deutsche Ausgabe. Mit 5 Abbildungen. Leipzig: Akademische Verlagsgesellschaft m. b. H. 1912. pp. 28. Price, M. 1.50.

This lecture, as the title implies, discusses the discovery of this remarkable element, but it does more than that. It takes up some of its more important properties and its decomposition products. The decomposition products of thorium and actinium are also considered. H. C. J.

TAFELN ZUM GEBRAUCHE BEI DER BESTIMMUNG VON BRECHUNGSINDICES nach der Methode der konstanten Deviation von 40°. Von J. F. EIJKMAN, Prof. a/d. Univeristät Gröningen. Gröningen: Gebroeders Hoitsema. 1909.

This book of tables has been compiled to facilitate the calculation of the indices of refraction of liquids when the method of constant deviation is employed. In this method the liquid whose refractive index is sought is placed in a hollow glass prism mounted on the table of a spectrometer and the deviation of the incident light is measured. Having determined this angular magnitude and knowing the refracting angle of the prism, the tables permit the index of refraction of the liquid to be determined with ease. It is hardly probable, however, that the chemist who has occasion to determine the refractive indices of many liquids will resort to the slow and troublesome method involving the use of the spectrometer when several excellent refractometers are on the market. For those who have no refractometer the method and tables of Eijkman will prove of value. FREDERICK H. GETMAN

HIGHER MATHEMATICS FOR CHEMICAL STUDENTS. By J. RIDDICK PARTINGTON, B.Sc., Fellow of Manchester University. With forty-four diagrams. New York: D. Van Nostrand Co. 1912. pp. 272. Price, $2.00.

The idea of a selection of mathematical material for the special needs of chemical students has much to recommend it, and has already been embodied in some excellent works, both in German (e. g., Nernst and Schoenfliess) and English (Miller). The proper medium between shallow superficiality and a mathematical rigor impossible of attainment by the average student of what is still largely a descriptive science is not easy to hit. The present work seems to be little but a series of selections from ordinary mathematical treatises with a few examples and illustrations from chemistry thrown in. For the unmathematically minded it is neither simple enough in its pedagogy nor suggestive enough of the real importance to him of a clear grasp of a few principles; the student who has sufficient aptitude to work through this book would get much the same results from his college courses in mathematics. B. B. TURNER

A CONCISE HISTORY OF CHEMISTRY. By T. P. HILDITCH. New York: D. Van Nostrand Co. 1911. pp. 250. Price, $1.25.

It is a familiar practice of examiners to ask the well-primed student to state *all that he knows* of (e. g.) the atomic theory—in twenty minutes. Just such breathless haste inspires the pages of this little book, in praise of which it must be admitted that the amount of facts, names, and dates compressed into its 85,000 or 90,000 words is quite amazing. As a history, in the sense of a work which might be put into the hands of the average thoughtful student to give him a clear connected idea of the development of chemical science, it can scarcely be recommended; twice the number of words on one-half the material would have given better results. But as a kind of pocket dictionary of the subject, to which the fully developed chemist may refer, not only for a date, but for very useful tables and pithy explanatory paragraphs, it is well worth buying. While it appears that the desire to "cram" for examinations was the leading object in compiling this work, it cannot be denied that its author shows judgment as well as remarkably wide reading in his choice of material, and has put the facts into suggestive condensations. The short tables of prominent living workers at the end of the book will help the student in his original reading. It is concise, but hardly history.

B. B. TURNER

THE CHEMICAL CONSTITUTION OF THE PROTEINS. By R. H. A. PLIMMER, D.Sc., Assistant Professor of Physiological Chemistry in, and Fellow of University College, London. In Two Parts, with Diagrams. Second Edition. Part I, Analysis. Monographs on Biochemistry, edited by R. H. A. PLIMMER, D.Sc., and F. G. HOPKINS, M.A., M.B., D.Sc., F.R.S. London, New York, Bombay and Calcutta: Longmans, Green & Co. 1912. pp. xii + 188. Price, 5s. 6 d.

The first edition of this monograph is so well and favorably known as to make unnecessary any comment on its general excellence. The second edition shows thorough revision and considerable enlargement over the first. The discussions, both of the hydrolysis of proteins and isolation and estimation of the resulting amino acids, and of the chemical constitution of these amino acids, are thorough in themselves and are supplemented by exceptionally complete bibliographies. The value of the work is still further enhanced by the inclusion of a very complete compilation of the analyses of products of hydrolysis of the various individual proteins, which has been brought so closely down to date as to include data published in 1911.

H. C. SHERMAN

THE PHYSIOLOGY OF PROTEIN METABOLISM. By E. P. CATHCART, M.D., D.Sc., Grieve Lecturer on Chemical Physiology in the University of Glasgow, Research Associate of the Carnegie Institution, Washington. Monographs on Biochemistry, edited by R. H. A. PLIMMER, D.Sc., and F. G. HOPKINS, M.A., M.B., D.Sc., F.R.S. London, New York, Bombay and Calcutta: Longmans, Green & Co. 1912. pp. viii + 142. Price, $1.25.

This volume, according to the author's preface, does not pretend to cover the whole literature of protein metabolism, but "consists rather of the discussion of the more important results published during the last decade and their bearing upon the work of the earlier investigators." The principal contents are: Digestion and Absorption of Proteins; Protein Regeneration; Feeding Experiments with Abiuret Products of Digestion; Deaminization; Influence of the Food on the Composition of the Tissues; Protein Requirements; Theories of Protein Metabolism; Starvation; Work; and a Bibliography of over 400 titles.

The book is, in the main, clearly and interestingly written and the material included is generally well digested and concisely presented.

On the other hand, it is surprising to see the work of Chittenden so inadequately presented, and to find discussions of the influence of muscular work on metabolism and of the protein-sparing action of carbohydrate and fat which do not mention the work of Atwater and Benedict on these problems, nor take cognizance of their important findings. Two of the most interesting sections of the book, dealing respectively with the influence of a diet of pure foodstuffs and with the fate of nitrogenous food after absorption, would be much modified by the results recently published by Osborne and Mendel and by Folin and Denis, respectively, which are mentioned only in short footnotes evidently added while the work was in press. Notwithstanding these omissions, the book will doubtless be very useful in bringing before the general worker, in nutrition or food chemistry, an interesting presentation of modern viewpoints, and in furnishing the special student with a convenient summary and selected bibliography of most of the more important literature to the end of 1910. H. C. SHERMAN

ANNUAL TABLES OF CONSTANTS.

"The second volume of the ANNUAL TABLES OF CONSTANTS, CHEMICAL, PHYSICAL AND TECHNOLOGY, will be sold to subscribers at $6.00, unbound, *provided the subscription is received before January 31, 1913.* For further information see the inside page of the cover of the November number of THIS JOURNAL.

INDEX TO VOL. XLVIII

AUTHORS

ABEGG, R., *Auerbach, F.* and *Luther, R.* Messungen elektromotorischer Kräfte galvanischer Ketten mit wässerigen Elektrolyten (Review)....... 382

Acree, S. F. On the mechanism of organic reactions........... 352

Ambler J. A. See *Johnson, T. B.*

Arrhenius, S. Conférences sur quelques thèmes choisis (Review). 548

" The molecular theory (Report).................. 536

Auerbach, F. See *Abegg, R.*

Auld, S. J. M. An introduction to quantitative analysis (Review).................................... 469

BALY, E. C. C. Spectroscopy (Review)...................... 549

Bates, P. H. See *Wig, R. J.*

Beckurts, H. and *Lüning, O.* Die Methoden der Massanalyse. II (Review)........................ 196

Berge, A. Die Fabrikationen von Bittersalz und Chlormagnesium (Review).. 261

Bigelow, S. L. Theoretical and physical chemistry (Review).... 548

Billiter, J. Die elektrochemischen Verfahren der chemischen Gross-Industrie. II (Review)...................... 97

Böttger, W. Stand und Wege der analytischen Chemie (Review).. 99

Brunel, R. F. See *Michael, A.*

CASH, G. See *Morse, H. N.*

Cathcart, E. P. The physiology of protein metabolism (Review). 553

Clarke, H. T. A handbook of organic analysis (Review)....... 100

Clarkson, S. S. See *Dyson, S. S.*

Comité International. Tables annuelles internationales de constantes et données numériques (Review). 467

Cooper, H. C. See *Holleman, A. F.*

Curie, Mme. Die Entdeckung des Radiums (Review) 551

DAVIS, W. A. and *Sadtler, S. S.* Allen's commercial organic analysis. VI (Review)........ 261

Dyson, S. S. and *Clarkson, S. S.* Chemical works (Review)..... 470

EIJKMAN, J. F. Tafeln zum Gebrauche bei der Bestimmung von Brechungsindices (Review)............... 551

Engler, C. Das Erdöl (Review) 472

GAUTHIER, D. See *Thomas, V.*
Getman, F. H. and *Gibbons, V. L.* Potentials of zinc in alcoholic solutions of zinc chloride 124
" and *Gilroy H. T.* A study of the refractive indices of solutions of the cadmium halides 138
Gibbons, V. L. See *Getman, F. H.*
Gilroy, H. T. See *Getman, F. H.*
Given, A. Methods for sugar analysis (Review) 469
Graham, M. A. A study of the change from violet to green in solutions of chromium sulphate 145
Grant, J. The chemistry of breadmaking (Review) 194
Guest, H. H. See *Johnson, T. B.*

HILL, A.J. See *Johnson, T. B.*
Hoff, J. H. van't. Die chemischen Grundlehren nach Menge, Mass und Zeit (Review) 265
Holland, W. W. See *Morse, H. N.*
Holleman, A. F. and *Cooper, H. C.* A text-book of inorganic chemistry (Review) 102
Howard, S. F. and *Jones, H. C.* The conductivity, temperature coefficients of conductivity and dissociation of certain electrolytes in aqueous solution at 35°, 50° and 65° 500

JACOBSON, C. A. and *Marchlewski, L.* Methods for determining neo- and allochlorophyll in the presence of one another 111
Jellinek, K. Das Hydrosulfit. I (Review) 98
Johnson, A. E. The analyst's laboratory companion (Review) 468
" *T. B.* and *Ambler, J. A.* Desmotropism in the pseudothiohydantoins 197
" and *Guest, H. H.* Hydantoins: The action of potassium thiocyanate on asparagine 103
" and *Hill, A. J.* Researches on pyrimidines: The action of potassium thiocyanate on primary halides 296
" and *Moran, R. C.* Researches on pyrimidines: The oximes of some thioglycollide compounds and their behavior on reduction 307

Johnson, T. B. and *Shepard, N. A.* Researches on pyrimidines: The action of hydroxylamine on 4-methyl-6-oxypyrimidine - 2 - oxalothio - glycollic acid. β-Mercapto-α-oximidopropionic acid..... 279
Jones, H. C. See *Howard, S. F., Springer, Jr., A.* and *Wightman, E. P.*
" *L. W.* The Beckmann rearrangement of hydroxamic acids. 1

KEANE, C. A. See *Lunge, G.*
Knox, J. Physico-chemical calculations (Review)............. 102
Kober, P. A. and *Sugiura, K.* The copper complexes of amino acids, peptides and peptones...... 383

LÜNING, O. See *Beckurts, H.*
Lunge, G. and *Keane, C. A.* Technical methods of chemical analysis. II (Review).................. 190
Luther, R. See *Abegg, R.*

MARCHLEWSKI, L. See *Jacobson, C. A.*
Merck, E. Annual report of recent advances in pharmaceutical chemistry and therapeutics. XXIV, 1910 (Review). 196
" Prüfung der chemischen Reagentien auf Reinheit (Review)...................................... 196
Michael, A. and *Brunel, R. F.* On the action of aqueous solutions of acids on alkenes......... 267
Moore, F. J. Experiments in organic chemistry (Review)....... 467
" Outlines of organic chemistry (Review).......... 382
Moran, R. C. See *Johnson, T. B.*
Morse, H. N., Holland, W. W., Myers, C. N., Cash, G. and *Zinn, J. B.* The osmotic pressure of cane sugar solutions at high temperatures 29
Myers, C. N. See *Morse, H. N.*

NICHOLS, E. H. See *Orndorff, W. R.*
Nowell, J. W. Action of heat on *p*-sulphamido-*o*-toluic acid.... 223

ORNDORFF, W. R. and *Nichols, E. H.* Octochloroindigo and some derivatives of tetrachloroanthranilic and tetrachlorophthalic acids................ 473

PARTINGTON, J. R. Higher mathematics for chemical students (Review)............................ 552

Pearce, J. N. and *Weigle, O. M.* Velocity coefficients of the reaction between ethyl iodide and silver nitrate in ethyl and methyl alcohols and mixtures of these solvents.............. 243
Planck, M. Ueber neue thermodynamische Theorien (Review). 551
Plimmer, R. H. A. The chemical constitution of the proteins. I (Review)................................ 553
Poulenc, C. Les nouveautés chimiques pour 1911 (Review)..... 102
Pring, J. N. Laboratory exercises in physical chemistry (Review).................................... 265

REIMER, M. and *Reynolds, G. P.* The reaction between organic magnesium compounds and cinnamylidene esters. IV. Reactions with methyl α-methylcinnamylidenacetate....................... 206
Reynolds, G. P. See *Reimer, M.*

SADTLER, S. S. See *Davis, W. A.*
Schwalbe, C. G. Die Chemie der Cellulose. II (Review)......... 192
Seidell, A. Solubility and distribution coefficients of thymol.... 453
Shepard, N. A. See *Johnson, T. B.*
Soddy, F. The chemistry of the radio elements (Review)....... 101
Spencer, J. F. An experimental course of physical chemistry. II (Review).................................. 195
Springer, Jr., A. and *Jones, H. C.* A study of the conductivity and dissociation of certain organic acids in aqueous solution at different temperatures. 411
Sugiura, K. See *Kober, P. A.*

THOMAS, V. and *Gauthier, D.* Notions fondamentales d'analyse qualitative (Review)........... 264
Thorpe, E. A dictionary of applied chemistry (Review):
  Vol. I, A–Che................................. 191
  Vol. II, Chi–Gou.............................. 259
Toch, M. Materials for permanent painting (Review).......... 262

WEIGLE, O. M. See *Pearce, J. N.*
Whymper, R. Cocoa and chocolate (Review)................. 95
Wig, R. J. and *Bates, P. H.* Tests of the absorptive and permeable properties of Portland cement mortars and concretes (Review)... 263

Wightman, E. P. and *Jones, H. C.* A study of the conductivity and dissociation of certain organic acids at 35°, 50° and 65° 320

ZINN, J. B. See *Morse, H. N.*
Zsigmondy, R. Kolloidchemie (Review) 470

SUBJECTS

2-ACETYLMETHYLMERCAPTO-4-METHYL-6-OXYPYRIMIDINE, 314; oxime, 316. *Johnson* and *Moran* 314
Acetylsalicylic acid, conductivity and dissociation of. *Springer* and *Jones* 435
Acetyltetrachloroindoxyl. *Orndorff* and *Nichols* 485
3-Acetyl-2-thiohydantoin-4-acetamide. *Johnson* and *Guest* 108
Alkenes, action of aqueous solutions of acids on. *Michael* and *Brunel* 267
Allo- and neochlorophyll in the presence of one another, methods for determining. *Jacobson* and *Marchlewski* 111
Allylmalonic acid, conductivity and dissociation of. *Springer* and *Jones* 425
Amino acids, peptides and peptones, copper complexes of. *Kober* and *Sugiura* 383
m-Aminobenzoic acid, conductivity and dissociation of. *Wightman* and *Jones* 344
Ammonium chromium sulphate (violet and green), conductivity and dissociation of. *Howard* and *Jones* 515
Anisic acid, conductivity and dissociation of. *Springer* and *Jones*. 436
Annual Tables of Constants 559
Asparagine, the action of potassium thiocyanate on. *Johnson* and *Guest* 103
Aspartic acid, action of potassium thiocyanate on. *Johnson* and *Guest* 110

BECKMANN rearrangement of hydroxamic acids. *Jones* 1
Benzenesulphonic acid, conductivity and dissociation of. *Wightman* and *Jones* 345
Benzilic acid, conductivity and dissociation of. *Wightman* and *Jones* 336
2-Benzoylmethylmercapto-4-methyl-6-benzoylmethoxypyrimidine. *Johnson* and *Moran* 312
2-Benzoylmethylmercapto-4-methyl-6-oxypyrimidine, 312; sodium salt, 314; oxime, 315; oxime hydrochloride, 315; phenylhydrazone, 317. *Johnson* and *Moran* 312

Benzylmalonic acid, conductivity and dissociation of. *Springer* and *Jones*.......... 426
Bromosuccinic acid, conductivity and dissociation of. *Springer* and *Jones*.......... 431
Butylmalonic acid, conductivity and dissociation of. *Springer* and *Jones*.......... 424

CADMIUM halides, refractive indices of solutions of. *Getman* and *Gilroy*.......... 138
Calcium bromide and chromate, conductivity and dissociation of. *Howard* and *Jones*.......... 517
Camphoric acid, conductivity and dissociation of. *Wightman* and *Jones*.......... 349
Cane sugar solutions at high temperatures, osmotic pressure of. *Morse*, *Holland*, *Myers*, *Cash* and *Zinn*.......... 29
Caprylic acid, conductivity and dissociation of. *Wightman* and *Jones*.......... 333
Carbamido-*o*-toluene-*p*-sulphonic acid, 230; ammonium and barium salts, 232. *Nowell*.......... 230
o-Chlorobenzoic acid, conductivity and dissociation of. *Wightman* and *Jones*.......... 338
Chromium sulphate, change from violet to green in solutions of. *Graham*.......... 145
Cinnamic acid, conductivity and dissociation of. *Springer* and *Jones*.......... 441
Cinnamylidene esters and organic magnesium compounds, reactions between. *Reimer* and *Reynolds*.......... 206
Conductivity and dissociation of certain organic acids at 35°, 50° and 65°. *Wightman* and *Jones*.......... 320
Conductivity and dissociation of certain organic acids in aqueous solution at different temperatures. *Springer* and *Jones*.... 411
Conductivity, temperature coefficients of conductivity and dissociation of certain electrolytes in aqueous solution at 35°, 50° and 65°. *Howard* and *Jones*.......... 500
Copper complexes of amino acids, peptides and peptones. *Kober* and *Sugiura*.......... 383
o-Coumaric acid, conductivity and dissociation of. *Springer* and *Jones*.......... 441
Cyanoacetic acid, conductivity and dissociation of. *Wightman* and *Jones*.......... 328
ω-Cyanomethyltetrachloroanthranilic acid. *Orndorff* and *Nichols*. 481

DESMOTROPISM in the pseudothiohydantoins. *Johnson* and *Ambler*.......... 197
Diacetyltetrachloroindoxyl. *Orndorff* and *Nichols*.......... 485

Dibromo-α-methyl-β-phenyl-γ-benzalbutyrophenone. *Reimer* and *Reynolds*........ 214
Dibromosuccinic acid, conductivity and dissociation of. *Springer* and *Jones*........ 432
Dichloroacetic acid, conductivity and dissociation of. *Springer* and *Jones*........ 421
Dichlorophthalic acid, conductivity of. *Wightman* and *Jones*.... 348
Diethylmalonic acid, conductivity and dissociation of. *Springer* and *Jones*........ 429
α,α-Diethyl-β-methyl-δ-benzalcrotonyl alcohol. *Reimer* and *Reynolds*........ 222
Diethyl 4-methyl-6-oxypyrimidine-2-oxalothioglycollate. *Johnson* and *Shepard*........ 284
1,2,4-Dihydroxybenzoic acid, conductivity and dissociation of. *Wightman* and *Jones*........ 343
Dimethylaminoazotetrachlorobenzene-*o*-carboxylic acid. *Orndorff* and *Nichols*........ 478
Dimethylmalonic acid, conductivity and dissociation of. *Springer* and *Jones*........ 427
4,6-Dinitro-2-aminophenol, conductivity and dissociation of. *Springer* and *Jones*........ 439
1,2,4- and 1,3,5-Dinitrobenzoic acids, conductivity and dissociation of. *Wightman* and *Jones*........ 341
2,6 - Dioxy - 4 - chloromethyl - 5 - phenoxypyrimidine. *Johnson* and *Hill*........ 303
2,6-Dioxy-4-mercaptomethyl-5-phenoxypyrimidine. *Johnson* and *Hill*........ 304
2,6-Dioxy-4-naphthoxymethyl-5-naphthoxypyrimidine. *Johnson* and *Hill*........ 306
2,6-Dioxy-4-phenoxymethyl-5-phenoxypyrimidine. *Johnson* and *Hill*........ 303
Dipotassium phosphate, conductivity and dissociation of. *Howard* and *Jones*........ 509
Dipropylmalonic acid, conductivity and dissociation of. *Springer* and *Jones*........ 430

ERRATA........ 382, 575
Ethyl α,α-dinaphthoxyacetoacetate, sodium salt of. *Johnson* and *Hill*........ 305
Ethyl α,γ-diphenoxyacetoacetate, sodium salt of. *Johnson* and *Hill*........ 301
Ethyl iodide and silver nitrate in ethyl and methyl alcohols and mixtures of these solvents, velocity coefficients of the reaction between. *Pearce* and *Weigle*........ 243
Ethylmalonic acid, conductivity and dissociation of. *Springer* and *Jones*........ 422

2 - Ethylmercapto - 4 - naphthoxymethyl - 5 - naphthoxy - 6 - oxy - pyrimidine. *Johnson* and *Hill*. 305
2 - Ethylmercapto - 4 - phenoxymethyl - 5 - phenoxy - 6 - oxypyrimidine. *Johnson* and *Hill*. 302

HYDANTOIN-4-ACETIC acid (malyureidic acid). *Johnson* and *Guest*. 109
Hydantoins: The action of potassium thiocyanate on asparagine. *Johnson* and *Guest*. 103
Hydrochloric acid, conductivity and dissociation of. *Howard* and *Jones*. 528
Hydrocinnamic acid, conductivity and dissociation of. *Springer* and *Jones*. 440
Hydroxamic acids, Beckmann rearrangement of. *Jones*. 1
m- and *p*-Hydroxybenzoic acids, conductivity and dissociation of. *Wightman* and *Jones*. 342
Hydroxyisobutyric acid, conductivity and dissociation of. *Wightman* and *Jones*. 331
γ-Hydroxytriphenylmethylbutyrolactone. *Reimer* and *Reynolds*. 214

ISOPROPYLMALONIC acid, conductivity and dissociation of. *Springer* and *Jones*. 423
Isovaleric acid, conductivity and dissociation of. *Wightman* and *Jones*. 332

LEAD acetate and chloride, conductivity and dissociation of. *Howard* and *Jones*. 521
Levulinic acid, conductivity and dissociation of. *Wightman* and *Jones*. 330

MALYUREIDIC acid. *Johnson* and *Guest*. 109
Mechanism of organic reactions. *Acree*. 352
Meconic acid, conductivity and dissociation of. *Wightman* and *Jones*. 337
β-Mercapto-α-oximidopropionic acid. *Johnson* and *Shepard*. 279
Metanilic acid, conductivity and dissociation of. *Springer* and *Jones*. 438
α-Methyl-β-benzyl-γ-benzalpropyl benzyl ketone. *Reimer* and *Reynolds*. 221
Methylethylmalonic acid, conductivity and dissociation of. *Springer* and *Jones*. 428
Methyl α-methylcinnamylidenacetate, reactions with organic magnesium compounds. *Reimer* and *Reynolds*. 206
4-Methyl-6-oxyprimidine-2-oxalothioglycollic acid, action of hydroxylamine on. *Johnson* and *Shepard*. 279

4-Methyl-6-oxypyrimidine-2-oximidothiopropionic acid. *Johnson* and *Shepard* 289
4-Methyl-6-oxypyrimidine-2-oximidothiosuccininc acid, sodium salt of. *Johnson* and *Shepard* 290
4-Methyl-6-oxypyrimidine-2-thiopyruvic acid. *Johnson* and *Shepard* 286
α-Methyl-β-phenyl-γ-benzalbutyrophenones, isomeric. *Reimer* and *Reynolds* 212, 217
Methylphenylbenzal-1,3-pentadiene. *Reimer* and *Reynolds* 219
Methylphenylbenzoylpropionic acids, isomeric, 216, 219; methyl ester, 216. *Reimer* and *Reynolds* 216
2-Methyl-1,1,3,5-tetraphenyl-4-pentene-1-ol. *Reimer* and *Reynolds* 213
Molecular theory (Report). *Arrhenius* 536

NAPHTHIONIC acid, conductivity and dissociation of. *Springer* and *Jones* 443
Neo- and allochlorophyll in the presence of one another, methods for determining. *Jacobson* and *Marchlewski* 111
Nickel acetate, conductivity and dissociation of. *Howard* and *Jones* 523
Nitric acid, conductivity and dissociation of. *Howard* and *Jones*. 529
m-Nitrobenzenesulphonic acid, conductivity and dissociation of. *Wightman* and *Jones* 346
o-, *m*- and *p*-Nitrobenzoic acids, conductivity and dissociation of. *Wightman* and *Jones* 338
1,4,2-Nitrotoluenesulphonic acid, conductivity and dissociation of. *Wightman* and *Jones* 347

OBITUARIES:
  Lecoq de Boisbaudran, Paul Émile 381
  Loeb, Morris 547
Octochloroindigo and some derivatives of tetrachloroanthranilic and tetrachlorophthalic acids. *Orndorff* and *Nichols* 473
Organic acids at 35°, 50° and 65°, conductivity and dissociation of certain. *Wightman* and *Jones* 320
Organic acids in aqueous solution at different temperatures, conductivity and dissociation of. *Springer* and *Jones* 411
Organic magnesium compounds and cinnamylidene esters, reaction between. *Reimer* and *Reynolds* 206
Organic reactions, mechanism of. *Acree* 352
Osmotic pressure of cane sugar solutions at high temperatures. *Morse*, *Holland*, *Myers*, *Cash* and *Zinn* 29
2-Oximido-4-methyl-6-oxypyrimidine. *Johnson* and *Shepard* 287

PEPTIDES, peptones and amino acids, copper complexes of. *Kober* and *Sugiura* 383

Phenylacethydroxamic acid, 6; benzoate and its sodium, potassium and silver salts, 7; acetate and its potassium salt, 10; propionate, 11; butyrate, 11; isobutyrate, 11. *Jones* 6
Phenylacetic acid, conductivity and dissociation of. *Springer* and *Jones* 422
Phenylpropiolic acid, conductivity and dissociation of. *Springer* and *Jones* 433
o-Phthalic acid, conductivity and dissociation of. *Springer* and *Jones* 442
Potassium carbonate, permanganate, sodium sulphate, chromium sulphate (violet and green) and nickel sulphate, conductivity and dissociation of. *Howard* and *Jones* 507
Potentials of zinc in alcoholic solutions of zinc chloride. *Getman* and *Gibbons* 124
Primary halides, action of potassium thiocyanate on. *Johnson* and *Hill* 296
Propionic acid, conductivity and dissociation of. *Wightman* and *Jones* 329
Pseudothiohydantoinacetic acid, 201; sodium, barium and active brucine salts, 203; hydrochloride, 202. *Johnson* and *Ambler*. 201
Pseudothiohydantoins, desmotropism in. *Johnson* and *Ambler* .. 197
Pyrimidines:
  Action of hydroxylamine on 4-methyl-6-oxypyrimidine-2-oxalothioglycollic acid. β-Mercapto-α-oximidopropionic acid. *Johnson* and *Shepard* 279
  Action of potassium thiocyanate on primary halides. *Johnson* and *Hill* 296
  Oximes of some thioglycollide compounds and their behavior on reduction. *Johnson* and *Moran* 307
Pyromucic acid, conductivity and dissociation of. *Springer* and *Jones* 432

REFRACTIVE indices of solutions of the cadmium halides. *Getman* and *Gilroy* 138
Report: The molecular theory. *Arrhenius* 536
Reviews:
  Analyst's laboratory companion, the. *Johnson* 468
  Analytischen Chemie, Stand und Wege der. *Böttger* 99
  Applied Chemistry, a dictionary. Vol. I, A–Che; Vol. II, Chi-Gou. *Thorpe* 191, 259
  Bittersalz und Chlormagnesium, die Fabrikationen von. *Berge* 261
  Bread-making, the chemistry of. *Grant* 194
  Brechungsindices, Tafeln zum Gebrauche bei der Bestimmung von. *Eijkman* 551
  Cellulose, die Chemie der. II. *Schwalbe* 192

Chemical Works. *Dyson* and *Clarkson* 470
Chemischen Grundlehren nach Menge, Mass und Zeit, die. *van't Hoff* 265
Cocoa and chocolate. *Whymper* 95
Commercial organic analysis, Allen's. VI. *Davis* and *Sadtler*. 261
Conférences sur quelques thèmes choisis. *Arrhenius* 548
Elektrochemischen Verfahren der chemischen Gross-Industrie, die. II. *Billiter* 95
Elektromotorischer Kräfte galvanischer Ketten mit wässerigen Elektrolyten, Messungen. *Abegg*, *Auerbach* and *Luther* . . . 382
Erdöl, das. *Engler* 472
Hydrosulfit, das. *Jellinek* 98
Inorganic Chemistry, a text-book of. *Holleman* and *Cooper* . . 102
Kolloidchemie. *Zsigmondy* 470
Massanalyse, die Methoden der. II. *Beckurts* and *Lüning* . . . 196
Mathematics for chemical students, higher. *Partington* 552
Nouveautés chimiques pour 1911, les. *Poulenc* 102
Organic analysis, a handbook of. *Clarke* 100
Organic chemistry, experiments in. *Moore* 467
Organic chemistry, outlines of. *Moore* 382
Painting, materials for permanent. *Toch* 262
Pharmaceutical chemistry and therapeutics, annual report of recent advances in, XXIV, 1910. *Merck* 196
Physical chemistry, an experimental course of. II. *Spencer*. 195
Physical chemistry, laboratory exercises in. *Pring* 265
Physico-chemical calculations. *Knox* 102
Portland cement mortars and concretes, tests of the absorptive and permeable properties of. *Wig* and *Bates* 263
Protein metabolism, the physiology of. *Cathcart* 553
Proteins, the chemical constitution of the. I. *Plimmer* 553
Qualitative, notions fondamentales d'analyse. *Thomas* and *Gauthier* 264
Quantitative analysis, an introduction to. *Auld* 469
Radio elements, the chemistry of the. *Soddy* 101
Radiums, die Entdeckung des. *Curie* 551
Reinheit, Prüfung der chemischen Reagentien auf. *Merck* . . 196
Spectroscopy. *Baly* 549
Sugar analysis, methods for. *Given* 469
Tables annuelles internationales de constantes et données numériques. *Comité International* 467
Technical methods of chemical analysis. II. *Lunge* and *Keane* 190
Theoretical and physical chemistry. *Bigelow* 548
Thermodynamische Theorien, über neue. *Planck* 551

SALICYLIC acid, conductivity and dissociation of. *Springer* and *Jones*...... 434
Sodium ferrocyanide, conductivity and dissociation of. *Howard* and *Jones*...... 506
p-Sulphamidobenzoic acid, conductivity and dissociation of. *Wightman* and *Jones*...... 345
p-Sulphamido-*o*-toluic acid, action of heat on, 223; preparation, 226; ammonium and potassium salts, 226. *Nowell*...... 223
p-Sulphamido-*o*-tolunitrile. *Nowell*...... 225
Sulphanilic acid, conductivity and dissociation of. *Springer* and *Jones*...... 438
Sulphosalicylic acid, conductivity of. *Springer* and *Jones*...... 436
p-Sulpho-*o*-toluic acid, acid ammonium and barium salts. *Nowell.* 227
Sulphuric acid, conductivity and dissociation of. *Howard* and *Jones*...... 530

TARTARIC acid, conductivity and dissociation of. *Wightman* and *Jones*...... 334
Tetrachloroanthranilic acid and some derivatives. *Orndorff* and *Nichols*...... 473
Tetrachloroanthranilic acid formalide, 480; acetate, 481. *Orndorff* and *Nichols*...... 480
Tetrachloroindoxylic acid acetate, 486; silver salt, 488. *Orndorff* and *Nichols*...... 486
Tetrachlorophenylglycine-*o*-carboxylic acid. *Orndorff* and *Nichols* 483
Tetrachlorophthalic acid, conductivity of. *Wightman* and *Jones.* 349
Tetrachlorophthalic acid, some derivatives of. *Orndorff* and *Nichols*...... 473
Tetrachlorophthaloxime, 494; sodium salt, 497; hydrate, 494; hydrate methyl ether, 492; acetate, 498. *Orndorff* and *Nichols* 494
Tetramethylethylene, action of aqueous hydrobromic acid on. *Michael* and *Brunel*...... 278
Thiodiglycolic acid, conductivity and dissociation of. *Wightman* and *Jones*...... 335
Thioglycollide oximes and their behavior on reduction. *Johnson* and *Moran*...... 307
2-Thiohydantoin-4-acetic acid. *Johnson* and *Guest*...... 108
2-Thio-4-naphthoxymethyl-5-naphthoxy-6-oxypyrimidine. *Johnson* and *Hill*...... 305
2-Thio-4-phenoxymethyl-5-phenoxy-6-oxypyrimidine. *Johnson* and *Hill*...... 302
Thymol, solubility and distribution coefficients of. *Seidell*...... 453
p-Toluenesulphonic acid, conductivity and dissociation of. *Wightman* and *Jones*...... 346
o-Tolunitrile-*p*-sulphone chloride. *Nowell*...... 225

Tricarballylic acid, conductivity and dissociation of. *Wightman* and *Jones* 336
Trichloroacetic acid, conductivity and dissociation of. *Wightman* and *Jones* 327
Trimethylethylene, action of aqueous hydrobromic acid on. *Michael* and *Brunel* 276

URANYL acetate, chloride, nitrate and sulphate, conductivity and dissociation of. *Howard* and *Jones* 524

VANILLIC acid, conductivity and dissociation of. *Springer* and *Jones* 437
Velocity coefficients of the reaction between ethyl iodide and silver nitrate in ethyl and methyl alcohols and mixtures of these solvents. *Pearce* and *Weigle* 243

ZINC in alcoholic solutions of zinc chloride, potentials of. *Getman* and *Gibbons* 124
Zinc acetate and nitrate, conductivity and dissociation of. *Howard* and *Jones* 519

FORMULAS

C_2-GROUP

2 II

C_2H_5I. Iodoethane. *Pearce* and *Weigle* 243

2 III

$C_2HO_2Cl_3$. Trichloromethanecarboxylic acid. *Wightman* and *Jones* 327
$C_2H_2O_2Cl_2$. Dichloromethanecarboxylic acid. *Springer* and *Jones* 421

C_3-GROUP

3 II

$C_3H_6O_2$. Ethanecarboxylic acid. *Wightman* and *Jones* 329

3 III

$C_3H_3O_2N$. Cyanomethanecarboxylic acid. *Wightman* and *Jones*. 328

3 IV

$C_3H_5O_3NS$. α-Hydroxyimino - β - mercaptoethane - α - carboxylic acid. *Johnson* and *Shepard* 288

C_4-GROUP

4 II

$C_4H_6O_6$. α,β-Dihydroxyethane-α,β-dicarboxylic acid. *Wightman* and *Jones* 334
$C_4H_8O_3$. α-Hydroxy-α-methylethane-α-carboxylic acid. *Wightman* and *Jones* 331

4 III

$C_4H_4O_4Br_2$. α,β-Dibromoethane-α,β-dicarboxylic acid. *Springer* and *Jones*........ 432

$C_4H_5O_4Br$. α-Bromoethane-α,β-dicarboxylic acid. *Springer* and *Jones*........ 431

$C_4H_6O_4S$. Di[carboxymethyl]sulphide. *Wightman* and *Jones*... 335

$C_4H_7O_4N$. α-Aminoethane-α,β-dicarboxylic acid (aspartic acid). *Johnson* and *Guest*........ 110

C_5-GROUP

5 I

C_5H_{10}. β-Methyl-β-butene. *Michael* and *Brunel*........ 276

5 II

$C_5H_4O_3$. Furane-2-carboxylic acid. *Springer* and *Jones*........ 432

$C_5H_8O_3$. γ-Ketobutane-α-carboxylic acid. *Wightman* and *Jones*. 330

$C_5H_8O_4$. (1) Propane-α,α-dicarboxylic acid. *Springer* and *Jones*. 422
  (2) α-Methylethane-α,α-dicarboxylic acid. *Springer* and *Jones*........ 427

$C_5H_{10}O_2$. β-Methylpropane-α-carboxylic acid. *Wightman* and *Jones*........ 332

5 III

$C_5H_6O_4N_2$. 2,5-Diketotetrahydro-1,3-diazole-4-acetic acid (malyureidic acid). *Johnson* and *Guest*........ 109

$C_5H_7O_2N_3$. 2 - Hydroxyimino - 6 - keto - 4 - methyl - 1,2,3,6 - tetrahydro - 1,3 - diazine. + ½H_2O. *Johnson* and *Shepard* .. 287

5 IV

$C_5H_6O_3N_2S$. (1) 5 - Keto - 2 - thiotetrahydro - 1,3 - diazole - 4 - acetic acid. *Johnson* and *Guest*........ 108
  (2) 2 - Imino - 4 - ketotetrahydrothiazole - 5 - acetic acid. HCl, Na + $3H_2O$, ½(Ba + H_2O). *Johnson* and *Ambler*.... 201

C_6-GROUP

6 I

C_6H_{12}. β,γ-Dimethyl-β-butene. *Michael* and *Brunel*........ 278

6 II

$C_6H_8O_4$. γ-Butene-α,α-dicarboxylic acid. *Springer* and *Jones* .. 425

$C_6H_8O_6$. Propane-α,β,γ-tricarboxylic acid. *Wightman* and *Jones*. 336

$C_6H_{10}O_4$. (1) α-Methylpropane-α,α-dicarboxylic acid. *Springer* and *Jones*........ 428
  (2) γ-Methylpropane-α,α-dicarboxylic acid. *Springer* and *Jones*........ 423

6 III

$C_6H_5O_5N_3$. 4,6-Dinitro-2-amino-1-hydroxybenzene. *Springer* and *Jones*........ 439

$C_6H_6O_3S$. Benzenesulphonic acid. *Wightman* and *Jones* 345

6 IV

$C_6H_5O_5NS$. 3-Nitrobenzene-1-sulphonic acid. *Wightman* and *Jones* 346
$C_6H_7O_3NS$. (1) 3-Aminobenzene-1-sulphonic acid. *Springer* and *Jones* 438
(2) 4-Aminobenzene-1-sulphonic acid. *Springer* and *Jones* 438

C_7-GROUP

7 II

$C_7H_4O_7$. 3-Hydroxy-1,4-pyrone-2,6-dicarboxylic acid (meconic acid). *Wightman* and *Jones* 337
$C_7H_6O_3$. (1) 2-Hydroxybenzene-1-carboxylic acid. *Springer* and *Jones* 434
(2) 3-Hydroxybenzene-1-carboxylic acid. *Wightman* and *Jones* 342
(3) 4-Hydroxybenzene-1-carboxylic acid. *Wightman* and *Jones* 343
$C_7H_6O_4$. 2,4-Dihydroxybenzene-1-carboxylic acid. *Wightman* and *Jones* 343
$C_7H_{12}O_4$. (1) Pentane-α,α-dicarboxylic acid. *Springer* and *Jones* 424
(2) α-Ethylpropane-α,α-dicarboxylic acid. *Springer* and Jones 429

7 III

$C_7H_4O_6N_2$. (1) 2,4-Dinitrobenzene-1-carboxylic acid. *Wightman* and *Jones* 341
(2) 3,5-Dinitrobenzene-1-carboxylic acid. *Wightman* and *Jones* 341
$C_7H_5O_2Cl$. 2-Chlorobenzene-1-carboxylic acid. *Wightman* and *Jones* 338
$C_7H_5O_4N$. (1) 2-Nitrobenzene-1-carboxylic acid. *Wightman* and *Jones* 338
(2) 3-Nitrobenzene-1-carboxylic acid. *Wightman* and *Jones*. 339
(3) 4-Nitrobenzene-1-carboxylic acid. *Wightman* and *Jones*. 340
$C_7H_6O_6S$. 2-Hydroxybenzene-1-carboxylic-4-sulphonic acid. *Springer* and *Jones* 436
$C_7H_7O_2N$. 3-Aminobenzene-1-carboxylic acid. *Wightman* and *Jones* 344
$C_7H_8O_3S$. 4-Methylbenzene-1-sulphonic acid. *Wightman* and *Jones* 346

7 IV

$C_7H_3O_2NCl_4$. 3,4,5,6-Tetrachloro-2-aminobenzene-1-carboxylic acid. *Orndorff* and *Nichols* 473
$C_7H_7O_4NS$. 4-Amide of benzene-1-carboxylic-4-sulphonic acid. *Wightman* and *Jones* 345

$C_7H_7O_5NS$. 3-Nitro-4-methylbenzene-1-sulphonic acid. *Wightman* and *Jones* 347

$C_7H_9O_3N_3S$. Amide of 3-acetyl-5-keto-2-thiotetrahydro-1,3-diazole-4-acetic acid. *Johnson* and *Guest* 108

C_8-GROUP

8 II

$C_8H_6O_4$. Benzene-1,2-dicarboxylic acid. *Springer* and *Jones* 442

$C_8H_8O_2$. Phenylmethanecarboxylic acid. *Springer* and *Jones* . . 442

$C_8H_8O_3$. Methyl ether of 4-hydroxybenzene-1-carboxylic acid. *Springer* and *Jones* 436

$C_8H_8O_4$. 3-Methyl ether of 3,4-dihydroxybenzene-1-carboxylic acid. *Springer* and *Jones* 437

$C_8H_{16}O_2$. Heptane-α-carboxylic acid. *Wightman* and *Jones* 333

8 III

$C_8H_2O_4Cl_4$. 3,4,5,6 - Tetrachlorobenzene - 1,2 - dicarboxylic acid. *Wightman* and *Jones* 349

$C_8H_4O_4Cl_2$. 3,6-Dichlorobenzene-1,2-dicarboxylic acid. *Wightman* and *Jones* 348

$C_8H_8O_5S$. 2-Methylbenzene-1-carboxylic-4-sulphonic acid. NH_4, ½Ba + H_2O. *Nowell* 227

$C_8H_9O_2N$. α-Hydroxyamino-α-keto-β-phenylethane (phenylacethydroxamic acid. *Jones* 6

8 IV

$C_8HO_3NCl_4$. Lactone of 3,4,5,6-tetrachlorochloro-2-hydroxyiminohydroxymethylbenzene-1-carboxylic acid. Na. *Orndorff* and *Nichols* 497

$C_8H_3O_2NCl_4$. Lactone of 3,4,5,6-tetrachloro-2-hydroxymethylaminobenzene-1-carboxylic acid. *Orndorff* and *Nichols* 480

$C_8H_3O_4NCl_4$. Lactone of 3,4,5,6-tetrachloro-2-hydroxyaminodihydroxymethylbenzene-1-carboxylic acid. *Orndorff* and *Nichols* 496

$C_8H_6O_2NS$. Chloride of 1-cyano-2-methylbenzene-4-sulphonic acid. *Nowell* 225

$C_8H_8O_2N_2S$. Amide of 1-cyano-2-methylbenzene-4-sulphonic acid. *Nowell* 225

$C_8H_8O_4N_2S$. 2 - [β - Keto - β - carboxyethyl]mercapto - 6 - keto - 4-methyl-1,6-dihydro-1,3-diazine. *Johnson* and *Shepard* 286

$C_8H_9O_4NS$. (1) 1-Amide of 2-methylbenzene-1-carboxylic-4-sulphonic acid. NH_4, ½Ba + H_2O. *Nowell* 230
(2) 4-Amide of 2-methylbenzene-1-carboxylic-4-sulphonic acid. K + ½H_2O, NH_4 + H_2O. *Nowell* 226

$C_8H_9O_4N_3S$. 2 - [β - Carboxy - β - hydroxyiminoethyl]mercapto - 6 - keto - 4 - methyl - 1,6 - dihydro - 1,3 - diazine. *Johnson* and *Shepard* 289

$C_8H_{10}O_2N_2S$. 2-[β-Ketopropyl]mercapto-6-keto-4-methyl-1,6-dihydro-1,3-diazine. *Johnson* and *Moran* 314

$C_8H_{11}O_2N_3S$. 2-[β-Hydroxyiminopropyl]mercapto-6-keto-1,6-dihydro-1,3-diazine. *Johnson* and *Moran* 316

C_9-GROUP
9 II

$C_9H_6O_2$. β-Phenylethin-α-carboxylic acid. *Springer* and *Jones* .. 433

$C_9H_8O_2$. β-Phenylethene-α-carboxylic acid. *Springer* and *Jones*. 441

$C_9H_8O_3$. β-[2-Hydroxyphenyl]ethene-α-carboxylic acid. *Springer* and *Jones* 441

$C_9H_8O_4$. Acetate of 2-hydroxybenzene-1-carboxylic acid. *Springer* and *Jones* 435

$C_9H_{10}O_2$. β-Phenylethane-α-carboxylic acid. *Springer* and *Jones*. 440

$C_9H_{16}O_4$. α-Propylbutane-α,α-dicarboxylic acid. *Springer* and *Jones* 430

9 IV

$C_9H_4O_2N_2Cl_4$. 3,4,5,6-Tetrachloro-2-cyanomethylaminobenzene-1-carboxylic acid. *Orndorff* and *Nichols* 481

$C_9H_6O_4NCl_4$. (1) 3,4,5,6-Tetrachlorobenzene-1-carboxylic-2-aminoacetic acid. + H_2O. *Orndorff* and *Nichols* 483
(2) Lactone of 3,4,5,6-tetrachloro-2-methoxyaminodihydroxymethylbenzene-1-carboxylic acid. *Orndorff* and *Nichols* 492

$C_9H_8O_6N_2S$. 2-[β-Keto-α,β-dicarboxyethyl]mercapto-6-keto-4-methyl-1,6-dihydro-1,3-diazine. *Johnson* and *Shepard*. 286

$C_9H_9O_6N_3S$. 2-[α,β-Dicarboxy-β-hydroxyiminoethyl]mercapto-6-keto-4-methyl-1,6-dihydro-1,3-diazine. Na_2. *Johnson* and *Shepard* 290

C_{10}-GROUP
10 II

$C_{10}H_{10}O_4$. β-Phenylethane-α,α-dicarboxylic acid. *Springer* and *Jones* 426

$C_{10}H_{14}O$. 3-Methyl-6-[α-methylethyl]-1-hydroxybenzene (thymol). *Seidell* 453

$C_{10}H_{16}O_4$. 1,1,2-Trimethyltetrahydro-R-pentene-2,5-dicarboxylic acid (camphoric acid). *Wightman* and *Jones* 349

10 III

$C_{10}H_{11}O_3N$. Acetate of α-hydroxyamino-α-keto-β-phenylethane. *Jones* 10

10 IV

$C_{10}H_3O_4NCl_4$. Lactone of 3,4,5,6-tetrachloro-2-acetoxyiminohydroxymethylbenzene-1-carboxylic acid. *Orndorff* and *Nichols* 498

$C_{10}H_5O_2NCl_4$. 4,5,6,7-Tetrachloro-3-hydroxy-1-acetyl-1-benzazole. *Orndorff* and *Nichols* 485

$C_{10}H_5O_3NCl_4$. Lactone of 3,4,5,6-tetrachloro-2-hydroxymethylacetylaminobenzene-1-carboxylic acid. *Orndorff* and *Nichols*. 481

$C_{10}H_9O_3NS$. 4-Aminonaphthalene-1-sulphonic acid. *Springer* and *Jones*.......... 443

C_{11}-GROUP

11 III

$C_{11}H_{13}O_3N$. Propionate of α-hydroxyamino-α-keto-β-phenylethane. *Jones*.......... 11

11 IV

$C_{11}H_5O_4NCl_4$. 4,5,6,7-Tetrachloro-3-hydroxy-1-acetyl-1 benzazole-2-carboxylic acid. Ag + H_2O. *Orndorff* and *Nichols*.......... 486

$C_{11}H_9O_3N_2Cl$. 5-Phenoxy-2,6-diketo-4-chloromethyl-1,2,3,6-tetrahydro-1,3-diazine. *Johnson* and *Hill*.......... 303

$C_{11}H_{10}O_3N_2S$. 5-Phenoxy-2,6-diketo-4-mercaptomethyl-1,2,3,6-tetrahydro-1,3-diazine. *Johnson* and *Hill*.......... 304

C_{12}-GROUP

12 II

$C_{12}H_{22}O_{11}$. Sucrose. *Morse*, *Holland*, *Myers*, *Cash* and *Zinn*.... 29

12 III

$C_{12}H_{15}O_3N$. (1) Butyrate of α-hydroxyamino-α-keto-β-phenylethane. *Jones*.......... 11
(2) Isobutyrate of α-hydroxyamino-α-keto-β-phenylethane. *Jones*.......... 11

12 IV

$C_{12}H_7O_3NCl_4$. 4,5,6,7-Tetrachloro-1,3-diacetyl-1-benzazole. *Orndorff* and *Nichols*.......... 485

C_{13}-GROUP

13 II

$C_{13}H_{14}O_2$. Methyl ester of ε-phenyl-β,δ-pentadiene-β-carboxylic acid. *Reimer* and *Reynolds*.......... 206

13 IV

$C_{13}H_{12}O_2N_2S$. 2-[β-Keto-β-phenylethyl]mercapto-6-keto-4-methyl-1,6-dihydro-1,3-diazine. Na (p. 314). *Johnson* and *Moran*.......... 312

$C_{13}H_{13}O_2N_3S$. 2-[β-Hydroxyimino-β-phenylethyl]mercapto-6-keto-4-methyl-1,6-dihydro-1,3-diazine. HCl. *Johnson* and *Moran*.......... 315

$C_{13}H_{16}O_6N_2S$. Diethyl ester of 2-[β-keto-α,β-dicarboxyethyl]mercapto-6-keto-4-methyl-1,6-dihydro-1,3-diazine. *Johnson* and *Shepard*.......... 284

C_{14}-GROUP
14 II

$C_{14}H_{12}O_3$. Hydroxydiphenylmethanecarboxylic acid. *Wightman* and *Jones*.. 336

C_{15}-GROUP
15 III

$C_{15}H_{13}O_3N$. Benzoate of α-hydroxyamino-α-keto-β-phenylethane. K, Na, Ag. *Jones*.. 7

15 IV

$C_{15}H_{11}O_2N_3Cl_4$. 3,4,5,6 - Tetrachloro - 4′ - dimethylaminoazobenzene-2-carboxylic acid. *Orndorff* and *Nichols*.............. 478

C_{16}-GROUP
16 II

$C_{16}H_{22}O$. γ - Hydroxy-δ-methyl-γ-ethyl-η-phenyl -δ,ζ- heptadiene. *Reimer* and *Reynolds*.. 222

16 IV

$C_{16}H_2O_2N_2Cl_8$. 4,5,6,7,4′,5′,6′,7′-Octochloroindigo. *Orndorff* and *Nichols*.. 489

C_{17}-GROUP
17 II

$C_{17}H_{16}O_3$. γ - Keto - β - methyl - α,γ - diphenylpropane - α - carboxylic acids, isomeric. *Reimer* and *Reynolds*............ 216, 219

17 III

$C_{17}H_{14}O_4N_2$. 5 - Phenoxy - 2,6 - diketo - 4 - phenoxymethyl - 1,2,-3,6-tetrahydro-1,3-diazine. *Johnson* and *Hill*.............. 303

17 IV

$C_{17}H_{14}O_3N_2S$. 5 - Phenoxy - 6 - keto - 2 - thio - 4 - phenoxymethyl-1,2,3,6-tetrahydro-1,3-diazine. *Johnson* and *Hill*........... 302

C_{18}-GROUP
18 II

$C_{18}H_{18}O_3$. Methyl ester of γ-keto-β-methyl-α,γ-diphenylpropane-α-carboxylic acid. *Reimer* and *Reynolds*.................. 216

$C_{18}H_{18}O_5$. Ethyl ester of α,γ-diphenoxy-β-ketopropane-α-carboxylic acid. Na. *Johnson* and *Hill*........................ 301

C_{19}-GROUP
19 IV

$C_{19}H_{18}ON_4S$. 2 - [β - Phenylhydrazone - β - phenylethyl]mercapto-6 - keto - 4 - methyl - 1,6 - dihydro - 1,3 - diazine. *Johnson* and *Moran*.. 317

$C_{19}H_{18}O_3N_2S$. 5 - Phenoxy - 2 - ethylmercapto - 6 - keto - 4 - phenoxymethyl-1,6-dihydro-1,3-diazine. *Johnson* and *Hill*....... 302

C_{21}-GROUP

21 IV

$C_{21}H_{18}O_3N_2S$. 6 - [β - Keto - β - phenylethyl] ether of 6 - hydroxy - 2 - [β - keto - β - phenylethyl]mercapto - 4 - methyl - 1,3 - diazine. *Johnson* and *Moran*.............................. 312

C_{23}-GROUP

23 II

$C_{23}H_{20}O_2$. Lactone of γ-hydroxy-β-methyl-α,γ,γ-triphenylpropane-α-carboxylic acid. *Reimer* and *Reynolds*.................. 214

C_{24}-GROUP

24 II

$C_{24}H_{22}O$. ε - Keto - δ - methyl - $\alpha,\gamma,\varepsilon$ - triphenyl - α - pentenes, isomeric. *Reimer* and *Reynolds*.......................... 212, 217

24 III

$C_{24}H_{22}OBr_2$. α,β - Dibromo - ε - keto - δ - methyl - $\alpha,\gamma,\varepsilon$ - triphenylpentane. *Reimer* and *Reynolds*.......................... 214

C_{25}-GROUP

25 III

$C_{25}H_{18}O_4N_2$. 5 - Naphthoxy - 2,6 - diketo - 4 - naphthoxymethyl - 1,2,3,6 - tetrahydro - 1,3 - diazine. *Johnson* and *Hill*........ 306

25 IV

$C_{25}H_{18}O_3N_2S$. 5 - Naphthoxy - 6 - keto - 2 - thio - 4 - naphthoxymethyl-1,2,3,6-tetrahydro-1,3-diazine. *Johnson* and *Hill*.... 305

C_{26}-GROUP

26 I

$C_{26}H_{24}$. δ - Methyl - ε - phenylmethyl - α,ζ - diphenyl - $\alpha,\gamma,\varepsilon$ - hexatriene. *Reimer* and *Reynolds*............................ 219

26 II

$C_{26}H_{22}O_5$. Ethyl ester of α,γ-dinaphthoxy-β-ketopropane-α-carboxylic acid. Na. *Johnson* and *Hill*..................... 305

$C_{26}H_{26}O$. ε - Keto - δ - methyl - γ -phenylmethyl - α,ζ - diphenyl - α-hexene. *Reimer* and *Reynolds*......................... 221

C_{27}-GROUP

27 IV

$C_{27}H_{22}O_3N_2S$. 5 - Naphthoxy - 2 - ethylmercapto - 6 - keto - 4 - naphthoxymethyl - 1,6 - dihydro - 1,3 - diazine. *Johnson* and *Hill*.. 305

C_{28}-GROUP

28 IV

$C_{28}H_{32}O_7N_4S$. Brucine salt of 2-imino-4-ketotetrahydrothiazole-5-acetic acid. *Johnson* and *Ambler*...................... 203

C_{30}-GROUP

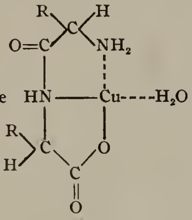
30 II

$C_{30}H_{28}O$. ε - Hydroxy - δ - methyl - α,γ,ε,ε - tetraphenyl - α - pentene. *Reimer* and *Reynolds* 213

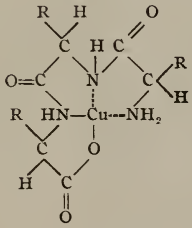
ERRATA

✓ p. 287, l. 4, the formula should be $C_9H_8O_6N_2S$.

✓ p. 386, l. 17, the formula should be



✓ p. 390, l. 8, the formula should be



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